

STANDARD OPERATING PROCEDURES MANUAL  
FOR THE  
DEPARTMENT OF ENVIRONMENTAL QUALITY  
WATER QUALITY MONITORING AND ASSESSMENT PROGRAM

Commonwealth of Virginia  
Department of Environmental Quality  
Water Quality Monitoring and Assessment  
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## Introduction to Water Quality Assessments Operating Procedures Manual

This document describes the routine operations and quality control activities performed by the Department of Environmental Quality (DEQ) in most of its ongoing data generating programs. Outlining procedures for sampling and field testing activities helps ensure that these procedures are standardized geographically across the state and between monitoring programs. The procedures described in this manual also help ensure that sampling precision, accuracy, representativeness, comparability and completeness of the data are obtained and documented. The sample collection procedures described in this document must be followed for all Water Quality Monitoring Programs unless the program is specifically covered under another SOP and/or Quality Assurance Project Plan that has been approved by WQMA QA Coordinator.

Many of the DEQ water quality monitoring programs have similar sample collection, field testing activities, and quality assurance requirements. Data generated from these programs must meet the needs of the data users. Comparability of data between DEQ's sampling programs and regional offices is an important quality objective.

# **1 Sampling Preparation**

Before going out, make a checklist of all routine material and equipment you will need for sampling to help you gather all the items needed. Make separate checklists for specialized sampling such as clean metals, sediment and boating sampling.

The checklist should include field data sheets showing sampling sites and QA sites if QC samples are collected, proper containers, preservatives, and labels, including QC samples, plus extra containers and labels. Equipment for field measurements, sampling devices, coolers, and ice. A topo map of the monitoring run and GPS unit to confirm site locations. Safety gear such as life jackets and safety vests as well as appropriate clothing and shoes. Bring the cell phone in case you need to get in touch of someone or emergency. Print the field data sheets and labels from CEDS for the scheduled run. Check that all sampling equipment is clean, in good working condition and the batteries are charged.

Let someone in your office where you will be, when you are expected to return and how to contact you if you are overdue.

Calibrate all field instruments according to WQM SOP and enter the calibration information into the calibration logsheet.

## **2 Sampling Requirements**

### ***2.1 Sampling equipment***

Sampling equipment has specific cleaning requirements based on its use in the field. Non-metallic materials, such as plastic or Teflon, are used whenever possible for the collection of samples for metals. For the collection of organic samples, non-organic or inert materials, such as stainless steel or Teflon, are used.

Never store or carry the spool in the bucket. Examine the equipment for obvious signs of dirt, rust or scratches and replace when necessary.

#### **2.1.1 Grab sampling equipment**

##### **2.1.1.1 Water matrices**

1. Rope on spool
2. An appropriately sized stainless steel bucket with a fitting for the bacteria sample bottle mounted on the inside, or as a substitute a suitable water sampling device (Van Dorn, Kemmerer, Labline, pump and hose or HDPE Nalgene bottle etc.)
3. Syringe, filter paper, filter holder etc.

### **2.1.1.2 Sediment matrices**

1. Rope on spool
2. Certified pre-cleaned glass jar with Teflon-lined lid
3. Teflon coated or plastic spoon, and stainless steel spoon
4. Appropriate dredge (such as Petit Ponar) depending on sediment type and depth of water
5. Appropriately sized stainless steel pan

## ***2.2 Sampling Equipment Preparation and Cleaning***

### **2.2.1 Water sampling equipment**

Daily:

1. Rinse sampling buckets at the end of the sampling day with analyte free water and allow to air dry at room temperature.
2. If a pump and hose apparatus is used, pump 5 gallons of analyte free water through the pump and hose system and completely drain.
3. If using a Kemmerer or Alpha Bottle sampling device follow the manufacturer's recommendations for cleaning those sampling devices using analyte free water.

Weekly:

1. Wash sampling buckets with lab grade soap (Liquinox or Alconox) at the end of each week using a brush, if necessary, to remove particulate matter or surface film.
2. Rinse thoroughly with tap water, then analyte free water, and allow to air dry at room temperature.

Monthly:

1. Pump 5 gallons of a 5% solution (5% solution consists of 1 quart of vinegar mixed with a 4 <sup>3</sup>/<sub>4</sub> gallons of water) through the hose and pump apparatus.
2. Pump 5 gallons of analyte free water through the hose and pump apparatus and completely drain.

Annually:

Replace hoses of pump and hose sampling devices.

### **2.2.2 Sediment sampling equipment**

1. Equipment should be washed thoroughly with clean scrub brushes using Alconox powdered or Liquinox liquid detergent.
2. Rinse with analyte free water.
3. Wash equipment using Citranox.
4. Rinse with analyte free water.
5. Rinse with pesticide grade Ethanol or Methanol to remove organic compounds.
6. Rinse thoroughly with analyte free water.
7. Dry equipment at room temperature in contaminant free air.
8. Visually inspect equipment for any contamination prior to storage.
9. Cover the clean equipment with clean aluminum foil until use.

### **2.3 Sample container handling and Preservation**

- Proper sample containers and sample preservation are essential to sample integrity. Refer to the DCLS laboratory catalog in CEDS for the appropriate preservation procedures. Samples not preserved properly may be rejected by DCLS.
- After sampling to make sure the lids were on tight to prevent contamination from water seepage in or out of the container.
- Sample containers should be stored with the tops securely fastened.
- In the field, samples should be iced to 4°C in a cooler immediately after collection. In the cooler, samples shall be placed upright and if possible, covered with ice in such a manner that the container openings are above the level of ice. Chlorophyll a filter pad samples will be placed in appropriately sized Ziploc bags and placed on top of the layer of ice. Ziploc bags containing filters should be oriented so that the sealed opening of the Ziploc bag hangs outside the cooler lid when the lid is closed. Bacteria sample

bottles should be stored in mesh bags, placed in coolers and surrounded with wet ice.

- Glass sample containers should be packed in bubble wrap or other waterproof protective materials to minimize accidental breakage.
- DCLS provides temperature bottles that they use to determine sample temperature upon arrival at DCLS. Make sure that every cooler used to ship samples to DCLS contains one of these bottles.
- Containers purchased by DEQ are parameter and program specific to meet agency and DCLS requirements for sample size and purity, container construction and material.
- Sample containers should be inspected and any torn, punctured or cracked sample containers discarded.
- Boxed or packaged sample containers should be dated by the regional office upon receipt and stocked on shelves with the oldest dated box/packages used first.

### Sample identification

Each sample container must be identified as to the station description, date, time, depth description, collector initials, parameter group code, sample type, container number, preservation used and volume filtered, if applicable. If more than one container is needed for a group code, each container collected for that group code must have a label with identical information in addition to an indication of 1 of 3, 2 of 3, 3 of 3, etc., as required.

The sample identification information should be printed on an adhesive Avery label and applied directly to the exterior of the container. In situations where the label will not adhere to the container, such as a cubitainer, the label may be affixed to a tag. The tag should be wired to the container in a way to prevent it coming off. The sample time must be hand written in indelible ink on labels with pre-printed station identification.

Labels for established sampling sites should be printed from CEDS. If the site is not established, the information must be hand printed with indelible ink on a blank adhesive label and then affixed to the container tag as necessary.

It is absolutely imperative that the actual sampling site match the labeling information.  
**Always check the labeling information against the actual site.**

Some sample types may have specific labeling requirements. Those requirements are detailed with those sampling guidelines.

Samples not labeled properly may be rejected by the laboratory.

## ***2.4 Chemical preservatives and reagents***

- Appropriate chemicals for equipment cleaning, and sample preservation are essential to sample integrity and accuracy.
- ACS reagent grade preservatives are required for sample preservation.
- Chemicals should be dated by the regional office upon receipt and upon opening of the container.

## ***2.5 Chemical preservatives and reagents disposal***

- Decontamination wastes must be segregated and disposed of properly.
- Soap solutions and waste tap/DI/analyte-free water can be poured down the drain.
- Solvents and weak acids used in cleaning may be diluted with water and poured down the sanitary sewer drain.
- Other waste solvents and concentrated, reagent grade preservative acids shall be handled as hazardous waste and must be collected and disposed of properly.

## **3 Field Sampling Procedures**

The section below details the collection of water and sediment samples utilized by almost all of the water quality monitoring programs. Further collection procedures for some miscellaneous specialty samples (e.g. VOCs, PAHs etc.) can be found in Appendix E.

### ***3.1 Use of protective gloves***

1. Gloves serve a dual purpose: 1) protecting the sample collector from potential exposure to sample constituents and 2) minimizing accidental contamination of samples by the collector.
2. Wearing protective gloves at all times while sampling is recommended, however, their use is not mandatory if: 1) the sample source is considered to be non-hazardous, or, 2) the samples will not be analyzed for trace (i.e. part per billion levels) constituents.
3. Latex or nitrile gloves may be used for common sampling conditions. The use of new, disposable, powder-free latex or nitrile gloves is required for clean metal sampling. Discarding the gloves is optional but in no circumstances should the gloves be reused for trace analysis sampling.

### ***3.2 Equipment Rinse***

When collecting aqueous samples, the sample collection equipment other than trace metals collection equipment shall be rinsed once with sample water before the actual sample is taken. For a sampling bucket, fill the bucket with site water, swirl the water around and dispose of the rinse water away from the sampling site. For sampling devices, clean the device inside and out by dipping it into and out of the site water or by washing with site water.

### ***3.3 Surface Water sampling***

#### **3.3.1 General**

1. Safety always comes first. All sampling should be conducted with the proper equipment and least amount of danger to field personnel. Use of safety cones and vests is recommended.
2. Site access will be left up to the sampling staff. Permission must be obtained from landowners before entering private property.

3. Care should be taken not to disturb the bottom when sampling. When entering a stream, always walk in an upstream direction.
4. If water samples and sediment samples are to be taken from the same area, the water samples must be taken first.
5. Surface water should always be collected facing upstream and in the center of main area of flow. Therefore, unless safety is an issue samples should be obtained from a bridge or instream.
6. Whenever possible, field measurements should be made in situ, not from bucket.
7. If utilizing discrete sampling bottles follow the manufacturer's instructions for maintenance, cleaning and use.
8. When there are obvious standing pools of water during low or no flow conditions do not collect samples or field measurements.

When collecting bacterial samples:

1. Do not rinse the bacteria sample bottle before collecting the sample.
2. Samples shall never be collected in an unsterilized sample container and transferred to a sterile container.
3. Be careful not to insert fingers into the mouth of the container or on the interior of the cap. Bacteriological sampling must always be collected as a grab sample and must never be composited.

### **3.3.2 Sampling from a bridge**

#### **3.3.2.1 General**

- Sample in the center of main flow from the safest side of the bridge and where contamination is least likely to occur.
- During rainy periods, avoid sampling where storm water runoff from the bridge can affect sample.
- Field parameters should be obtained immediately.
- In situations where field parameters are obtained from the bucket, all water samples must be collected prior to inserting the probe in the bucket.

### **3.3.2.2 Collection of samples with a stainless steel bucket modified for the collection of bacteria samples**

1. Lower the bucket into the center of main flow facing into the current and carefully rinse the bucket with ambient water 1-2 times. Raise the bucket after rinsing.
2. Remove the cap on the bacteria sample bottle and place the bottle into the rubber tubing on the inside of the bucket.
3. Place the rope through the clip located on the side of the bucket.
4. Slowly lower the bucket into the center of main flow. Once sufficient sample has been obtained, jerk the rope to free the rope from the clip and pull the bucket up toward you. The bacteria sample bottle will fill sufficiently.
5. Remove the bacteria sample bottle from the rubber tubing and cap it. Do not pour additional sample into the bacteria sample bottle or dip the bacteria sample bottle into the bucket to increase the volume of the sample.
6. If the volume of sample exceeds the mark on the bacteria sample bottle, pour off sufficient sample so the volume is approximately equal to or above the mark on the bottle shoulder and securely cap and label the container.
7. If a chlorophyll sample will be collected, follow the steps described in Section 2.5 prior to collecting any further samples.
8. Pour the samples directly from the bucket into any additional containers to be collected and cap them. Do not fully fill the containers, leave approximately one inch of air space in the bottles.
9. Add appropriate preservation as described in the DCLS catalog in CEDS. Note: the preservative also can be added to the bottles in the lab.
10. Put the chlorophyll filters separately into Ziploc bags, close the bags and place them in the cooler on top of the wet ice. Make sure the opening of the bag containing the chlorophyll filter hangs out of the cooler when the cooler lid is closed. Place the bacteria sample into the mesh bag and surrounded with wet ice.

11. Place all remaining sample containers into a cooler and place them in wet ice.

### **3.3.3 Sampling from a boat**

#### **General**

Bacterial samples need to be grabbed from the water into the direction of the current, and not from a pump and hose. Do not contaminate the sterile bottle by touching the inner surfaces of the bottle or cap.

Collect water samples before collecting sediment samples.

Make sure that hose is adequately marked to ensure accurate readings of the depth of the hose intake.

If possible, sample away from the engine in the direction of the current.

#### **3.3.3.1 Collection of samples with a pump and hose**

There are two methods that may be utilized to ensure a sufficient volume of water is allowed to flow through the hose to clear it:

##### **1) Air Bubble method:**

Rinse the pump and hose using the air bubble method by turning the pump on with the hose intake out of water to draw air into the hose. Then turn the pump off and lower the hose to the desired sampling depth. Turn the pump back on and watch for the air to completely exit the hose then let the pump run for 30 seconds before rinsing and filling the sample containers.

##### **2) Calculation of clearing time:**

Calculate the volume of the hose in gallons:

$$(r/12)^2 * 3.14 * L * 7.48 = V \text{ where}$$

r = radius (inches) of hose inner diameter

L = length (feet) of hose

V = volume (gallons)

Determine pump capacity (gallons per minute pumped) from the pump specifications.

Calculate time to flush hose:  $V/(gpm) = \text{time}$

Gpm = gallons per minute pumped

Time = minutes to flush hose

Multiply the time by 1.25 as a minimum clearing time for the hose.

**Note: Each time a new length or diameter of hose or pump is installed, the clearing time needs to be calculated in the above manner to ensure the waiting time is sufficient to clear the hose.**

When sampling close to the surface make sure the hose does not come out of the water and inadvertently pull some surface skim water through the hose.

Lower the hose to the desired depth, turn on the pump and wait the time calculated to clear the hose or for the bubble to clear from the hose to adequately rinse the hose before filling the containers.

After filling the sample containers, filter and preserve the sample as required. Check the containers and label for the correct station, date, time, depth, and sample type and put the appropriate labels on all samples before collecting another set of samples. Place filter in Ziploc bags and put the bags on the top of ice. Place all the sample containers in a cooler and surround the sample containers with wet ice.

### **3.3.3.2 Secchi disk**

1. Use a Secchi disk measuring 20 cm in diameter and attached to a line or chain marked in 0.1 m increments with paint or tape. **Note the marks need to be checked once a year for accuracy.**
2. Lower the Secchi disk into the water on the shaded side of the boat until the black and white quadrants are no longer distinguishable. **Do not wear sunglasses while obtaining this reading.**
3. Note the depth at which the quadrants were no longer distinguishable and then raise the disk until the quadrants are again distinct.
4. The recorded Secchi depth is the average of the two depths to the closest 0.1 m.

### **3.3.3.3 Light Attenuation**

**LICOR sensors need to be recalibrated every 2 years. Optimally, rotation of sensors should occur to allow only a single year of use in the field. However, no sensors will be utilized in the field for periods greater than 2 years. The Photo Diodes will degrade even when the sensors are not deployed in the field therefore each region will need to track purchases and recalibration dates accordingly. Additionally, regions need to track the dates sensors are utilized in the field. Purchases/recalibrations and utilization dates should be tracked for each sensor utilizing a LICOR sensor tracking sheet. The tracking sheets should be kept in a logsheet at each region.**

**The LICOR instrument requires an air or water multiplier for each sensor depending on the media it will be utilized in. The multiplier is the calibration coefficient for each sensor and is specified on the calibration documentation for each sensor. While the multipliers are stored in the data logger and do not need to be entered prior to each use, a new multiplier is required when the sensors are replaced and when the sensors are returned from the manufacturer after recalibration.**

**A. Entering multipliers/ initial set up for LI-1400:**

1. With the front panel face up and the display at the top, connect the light sensor into the BNC connector I1 located on the top left of the LI-1400 unit and the underwater sensor into the BNC connector I3 located on the top right of the LI-1400 unit.
2. Turn on the instrument by pressing the key labeled **ON**.
3. Press the key labeled **SETUP** on the data logger.
4. Select **CHANNELS** and press **ENTER**.
5. Using the right or left arrow keys select **I1=light**. Press **ENTER**.
6. Pressing the shift key to access the alpha characters on the numeric key pad (press shift once for the upper character or twice for the lower character) type **QUANTUM** for the description. Press **↓**.
7. Type in the multiplier for use in air from the tag attached to the air sensor or from the most recent certificate of calibration. Press **ENTER**.
8. Type **SA** for the label. Label is a two character alpha numeric code. **Channel 1 is SA** for surface air, **Channel 2 is UU** for underwater up. Press **↓**.
9. The LED will display **ave=** number. **Ave** is the number of seconds that the data logger will calculate a running average. Use the number keys to set the averaging time to 5 seconds. Press **↓**.
10. Use the right or left arrow to set the Log Routine to **none**.
11. Press **Esc** twice to return to the setup menu.
12. Complete steps 3-8 for channel 2 entering the water multiplier in step 7 for the depth sensor.
13. Press the **View** key and use the left and right arrow to toggle to New Data. Press **ENTER**.
14. Use the left and right arrow key to toggle the display until channel I1I is displayed. The LI-1400 is now configured to display the running average of the 5 previous seconds' instantaneous values of the quantum sensor and is now ready for use.

**B. Enter multipliers/initial set up for LI-1000:**

1. With the front panel face up and the display at the top, connect the light sensor into the BNC connector located on the top left of the LI-1000 unit and the underwater sensor into the BNC connector located on the top right of the LI-1000 unit.

2. Turn on the instrument by pressing the key labeled **FCT ON**.
3. Press the key labeled **CFG** on the data logger.
4. The LED will display **Mode is INST**. If the LED displays **LOG**, press the arrow key until the LED displays **INST** then press enter.
5. The LED will display **Ch1 is LIGHT**. If not, press the arrow key until the LED displays **LIGHT** and press enter.
6. The LED will display **range=A**. Using range=A, the data logger automatically sets the range to cover the widest input signal range with the best resolution. If not, press the arrow key until the LED displays **A**, then press enter.
7. The LED will display **mult = number**. The multiplier is the calibration coefficient for each sensor and is specified on the calibration documentation for each sensor. Enter the correct air multiplier number for the sensor that is attached to channel 1 (Deck sensor) using the number keys, then press enter.
8. The LED will display **Label = SA**. **Label** is a two character alpha numeric code. **Channel 1 is SA** for surface air, **Channel 2 is UU** for underwater up. Press enter after each code to confirm.
9. The LED will display **ave= number**. **Ave** is the number of seconds that the data logger will calculate a running average. Use the number keys to set the averaging time to 5 seconds then press enter.
10. The LED will display **ch 2 is LIGHT**. Complete steps 1-8 for channel 2 entering the water multiplier in step 6 for the depth sensor.
11. The LED will display **ch 3 is off**. Press enter until the LED displays **1A** followed by a series of numbers. The datalogger is now configured to display the running average of the 5 previous seconds' instantaneous values of the quantum sensor and is now ready for use.

### C. Data Collection:

1. Visually inspect LICOR meter probes and connections.  
Check battery level and ensure probes are positioned properly on deck and subsurface mountings.
2. Connect the deck sensor cable to the BNC connection on the top left of the data logger.
3. Secure the small deck sensor in an unobstructed area on the vessel.
4. Run the end of the cable for the underwater sensor to the data logger and connect the end of the underwater sensor to the BNC connector on the top right of the data logger.
5. Attach sufficient weight to the underwater sensor frame such that the sensor remains upright as it is lowered to depth.
6. On the sunny side of the boat, lower underwater sensor to depth just below the surface ensuring that the probe will not rise out of the water with wave action (Note: the depth for this reading is recorded as 0.1 meter in WQM).
7. Turn the instrument ON.

8. Obtain profile. Report values in whole numbers except for the last depth of the profile, for this observation report values in tenths.
  - At each depth a light attenuation reading is obtained from the deck sensor as well as from the water sensor.
  - Take initial readings with the deck sensor and just below the surface with water sensor.
  - Take second water sensor reading at depth of 0.5 meters.
  - Take successive water sensor readings at 0.5 meter increments.
  - Continue the profile until the underwater sensor displays either a value of approximately 10 micro Einsteins or a depth value that is 20% of the surface depth value.
  - Allow a minimum of 5 seconds between readings (to create a 5-second average value).
  - If the LICOR instrument is being used as a data logger, depress the “enter” key with each reading.
9. When profile is complete, turn the instrument OFF.
10. Record data on Licor Attenuation Sheet and transmit to CBO at the end of the month, along with the other field documentation sheets.

#### **3.3.3.4 Vacuum Filtering Method (In-Line Filtering)**

Some samples may require filtration utilizing an in-line manifold system. Current filtration techniques provide both the dissolved and particulate components of nitrogen and phosphorus and chlorophyll a. Filtering should be conducted as soon as possible after collection but no later than 2 hours after sample collection to prevent the biological and chemical processes occurring in the sample from significantly changing the analytical results. Currently regions conducting in-line filtering use a system consisting of 3-4 filtering stacks inter-connected by PVC pipes and connected by rubber tubing to a vacuum pump on one end and catch flasks at the other. Each filter stack has a bell (tower), frit (base) and a valve that enables the user to close off the vacuum to each individual filtering unit. Some regions have an unused stack used as a pressure release valve allowing the user to “bleed” off the excess pressure for easier removal of the filters from the base. The pump is connected to a 12-v battery power source.

##### **I. Supplies needed:**

###### **A. Filter stacks and filters:**

###### **1. PNC samples:**

- a. Filtering stack: Pall Gelman 25 mm 200 ml filter funnel and base (or equivalent).
- b. Filters: muffled 25 mm diameter, 1.0 um pore-sized Gelman type A/E glass fiber filters (see instructions below for muffling process). Prepare one filter for each sample to be analyzed and at least one additional filter per

sampling event to be submitted as a dry filter. The dry filters are utilized by DCLS for the determination of background carbon on the filters.

2. PP and Chlorophyll a samples:

- a. Filtering stack: Pall Gellman magnetic 300 ml filter funnel and base (or equivalent)
- b. Filters: 47 mm, 0.7 um pore-sized Whatman GF/F filters. One filter per PP sample to be collected and 1-3 filters per Chlorophyll a determination. 1-2 Dry filters must also be sent to the lab for a check for the possibility of background contamination.

B. Ancillary supplies:

1. 1-3 rinsing bottles filled with fresh DI water
2. Stainless steel forceps
3. Graduated cylinders – 200 ml, 100 ml and 50 ml graduated cylinders each of which are notched at the 200, 100 or 50 ml mark ensuring accurate delivery of 200 ml, 100 ml and 50 ml volumes of sample.
4. One Petri dish each per PNC and PP sample collected
5. One piece of foil per chlorophyll sample
6. One 250 ml plastic bottle per NTNP sample needed and an additional 250 ml bottle for additional collection of dissolved nutrients as needed to ensure adequate volumes of NTNP sample.
7. One sample tag and/or label per sample collected.

C. Pump and hose or other approved water collection apparatus

II. Preparation

Preparation for the filtering process includes: 1) Muffling 25 mm diameter glass fiber filters utilized for PNC (Particulate Nitrogen and Particulate Carbon analysis), 2) Acid washing the towers, graduated cylinders and plastic sample bottles and any reused 250 ml plastic NTNP bottles used in the filtering process, 3) rinsing the forceps with DI water and 4) collecting all the necessary supplies needed to properly identify the samples and ensure the delivery of uncontaminated, dry filter samples to DCLS.

A. Filter Muffling:

1. PNC filters must be muffled prior to their use to burn off as much background Carbon and nitrogen as possible. The filters are easily recontaminated with the opening and closing of the desiccators and therefore should not be carried over more than 30 days.
2. Place the required number of filters on an aluminum foil tray or in a porcelain crucible. One filter is required for each sample to be collected and one to two additional dry muffled filters are required by

DCLS for the determination of background carbon. It is advisable to muffle extra filters to allow the filtration of additional sample in the case of accidental loss.

3. Place the tray or crucible containing the filters in the muffle furnace, close and latch the door.
4. Set the furnace to 500 Celsius degrees.
5. Bake the filters for 15 minutes. **Do not over-bake or under-bake the filters.**
6. After 15 minutes, remove the filters from the furnace and allow them to cool in a desiccator for several hours.
7. Place the filters in a plastic snap-lid box with desiccant.
8. Replace/recharge desiccant as needed (usually when the dark blue color of the gel lightens to a pale blue).

B. Cleaning Filtration Equipment:

**Do not use detergent to clean filtering equipment or the sample bottles utilized for the collection of filtered samples (filtrate) as detergents can contain contaminants.**

1. Take all towers, graduated cylinders and tweezers and put them in the lab for cleaning.
2. Observe all safety precautions.
3. All safety measures necessary with the use of acid must be enforced. This includes the use of skin protection, such as rubber gloves, full-face shield, apron and footwear, as well as rinsing in an adequately ventilated area.
4. Clean one piece at a time.
5. Rinse all towers with DI water, strip them with 25 ml of 10% HCL and rinse 3 times again with DI water. A brush may be needed to remove any remaining sediment.
6. Rinse and strip the graduated cylinders in the same manner as the towers using approximately 10% of the total volume of graduated cylinder of 10% HCl using a brush if needed to remove any remaining sediment.
7. After use in the field, water will be trapped in the filtering apparatus. Use the flexible tube from the water collection tank to suck up water from inside the towers. Disconnect the water collection tank, empty it and reconnect.
8. Store the clean filtration equipment in a manner that prevents contamination (e.g. covered in aluminum foil or plastic).
9. Rinse all utensils with DI water 3 times.
  - Do not use HCl on metal utensils as it will promote the formation of rust.
10. Acid wash all reused plastic bottles and their caps that will be utilized in the collection of filtered samples with 10% HCl and triple rinse with DI water prior to their use in the field. Triple rinse any new bottles that

have been stored with their lids on with DI water. Replace the caps to seal the bottles until their use.

#### C. Manifold Set-up:

1. Connect the rubber tubing on the right side of the PVC manifold to outflow valve of the vacuum pump.
2. Connect the rubber tubing on the left side of the PVC manifold to the catch flasks.
3. Connect the catch flasks tubing to intake valve the vacuum pump.
4. Slide rubber stoppers onto the bases of PNC and PP towers.
5. Rinse all towers and bases thoroughly with DI water.
6. Secure bases into PVC manifold by firmly pressing stoppers into PVC openings leaving one opening available to “bleed” off excess pressure.
7. Place towers (funnels) onto bases.
8. Connect the vacuum power pump to the battery.
9. Close off all valves, turn on the pump and adjust the pressure to 10 psi. Turn off the pump – it is now ready for use.

### III. Filtration of Samples

#### A. Sample Collection.

1. Using a pump and hose (or an appropriately cleaned sampling device), rinse an acid washed and DI rinsed container such as a 2 L HDPE bottle or ½ gallon container with sample water. Fill the sample container with the sample including a sufficient quantity of water to filter more than one sample should it become necessary.

#### B. Equipment rinse:

1. Thoroughly rinse the inside of surface bells (filtration towers) with DI water (stored in a high-density polyethylene container).
2. Turn the towers upside down and rinse the area that connects to the base as it will contact the filter and is a potential site of contamination.
3. Rinse frits (base) with de-ionized water including the stems of the PP bases to prevent contamination to the filtrate in the 250 ml NTNP bottles.
4. Set up tower and base for filtering.
5. Ensure that there are catch flasks on line between the manifold and the vacuum source.
6. Connect vacuum power pump to battery.

#### C. Filtering

1. Place filters on bases.  
Using clean forceps and gripping on the filter edges, transfer a 47-mm Whatman 0.7 GF/F glass fiber filter onto the bases for PP/Chlorophyll

filtration and a muffled 25-mm filter for PNC. Replace each filtration tower on its base upon completion of the filter transfer.

**-Note:** be sure that PNC filters are “muffled” prior to use and place them grid side down. Place PP and chlorophyll filters on the filter tower in the same direction as they come out of the box.

- Discard any filters if they are dropped or the surface is scratched.

2. Place clean NTNP bottles under the PP bases:  
250 mls of filtered sample (filtrate) is required for the Dissolved nutrient analyses (NTNP sample). Depending on the amount of particulate/algae suspended in the sample, 100-250 mls are typically filtered through the PP filters. If less than 250 mls will be filtered through a single PP filter, place a second 250 ml bottle under another filter stack set up for a 47 mm filter use the second bottle to top off the sample.
3. Rinse graduated cylinders with sample:  
Mix sample thoroughly by shaking or tilting the plastic sample container vigorously, then rinse graduated cylinders with sample 1-2 times.
4. Transfer sample to towers:  
**Note:** - The volume of sample filtered will depend on amount of particulate matter/algae in the sample.  
- If the towers are color coded with tape, towers with green tape are used for PP samples and the blue for PNC samples.

- a. Thoroughly mix sample water and transfer a known volume quickly from containers to graduated cylinders and from cylinders to filtration towers to prevent settling of contents.

In cases where sample is turbid, start with a small volume and add 50 ml increments of sample until sample barely passes the filter (with pump on), or until the filter is well colored.

1. Use 300 ml for Chla filters.

Because the laboratory has to have enough concentrated chlorophyll to obtain a spectrophotometric reading, the field crew may need to utilize more than 1 filter to achieve the desired amount of chlorophyll. The volume of sample filtered in combination with the color of the filter will determine how many filters should be utilized. In general, if you have filtered 300 ml – 1 L of sample and have green color on the filter, you may use just that 1 filter. If you have filtered less than 300 ml of sample and have color other than green, you will need to filter 1 to 2 more filters. Be sure to filter the same volume in each of the successive filters (e.g. if the first filter processed 50 ml of sample and was brown in color, you will need to filter 2 more filters using 50 ml of sample each).

2. The usual volume filtered for PP is 250 mls (200 - 300 mls) and 100 mls (100 - 150 mls) are filtered for PNC.

A greater or lesser volume may be filtered depending on sample turbidity. In general PNC volumes should measure 50% of the volume filtered for PP.

b. Turn pump on.

- **Keep the vacuum below 12 psi of Hg (10 psi of Hg is preferable).**
- **Limit filtration duration to 10 minutes or less.**

These procedures must be followed to avoid cell damage during filtration and loss of chlorophyll into the filtrate. If it will take longer than 10 minutes to filter the selected sample volume, discard filter and remaining sample in bell, rinse the filtration apparatus and start again using a lesser sample volume.

c. Add MgCO<sub>3</sub> to last 25 ml of Chla sample.

**Note: If using the filtrate of the Chlorophyll sample for dissolved nutrients, be sure to remove the NTNP bottle from under the base prior to this step.** Shake to re-suspend the MgCO<sub>3</sub> and add approximately 1 ml of concentrated MgCO<sub>3</sub> - Laboratory grade - (prepared in a 1 g MgCO<sub>3</sub> to 100 ml of deionized water ratio) to the last 25 ml (approximately) of sample filtered in the filtration bell. This is equivalent to less than 1 mg of MgCO<sub>3</sub> per 15 ml extract.

d. Close valves or turn off pump to remove filtration vacuum.

Close valves just prior to filters being completely dry but dry enough to ensure none of the filtered material will be lost when the filter is folded for storage.

If filter pads are not “colored”, continue mixing, measuring and adding known volumes of sample water to each tower until the filters turn color.

e. Bleed excess pressure off.

Open valve to the PVC opening that does not have a filter stack on it.

f. Open the vacuum valves of the stacks slowly.

Close each valve after the sample filters through each tower.

g. Rinse forceps with DI water

h. Remove filters from base.

1. Fold the filter in half using forceps, being careful not to touch or disturb the particulate material on the surface of the filter.
2. Place Chlorophyll filter pads on a square of aluminum foil.  
If multiple filter pads are used for chlorophyll analysis, they must be packaged as one sample. Either wrap all filter pads in one piece of foil or wrap all separate foil packages together with one piece of foil.
3. Place PP filters in Petri dishes and sealed them (do not use aluminum foil as this may contaminate the filters). If using color coded tape, code PP dishes with green tape and PNC filters in Petri dishes sealed with blue tape.

i. Record the volume filtered.

Record the volume filtered on the sample tag (or label) and the WQM field sheet.

**All volumes MUST be recorded on the sample tag (or label) and the EDT field sheet.**

j. Remove NTNP bottle from PP cylinder and cap tightly.

**Note: The filtrate bottle should be filled to the bottom of the neck** If there is not enough filtrate, more sample needs to be filtered. In such an event, the “used” filters must be removed, placed in a Petri dish (only the first filter will be put in the Petri dish and analyzed), a new filter must be placed on the tower, and additional sample (after mixing) must be filtered. If the filters are being clogged very quickly due to large amounts of solids in the sample, continue replacing the clogged filters and add sample water as necessary.

- Pour filtrate from the bottle to rinse the cap.

**Note: There have been some problems with filling the filtrate bottles to the proper volume. Common causes for these problems are:**

- The old filter was not removed, water would not flow through, water in the tower and filter pad had to be thrown away and the process started again (filtrate was not contaminated and could be saved).
- New filter was not placed in tower, so sample water just poured into filtrate bottle. Bottle was contaminated and filtrate had to be thrown away (used filter pad was already in Petri dish and could be used).

k. Label samples.

- Place a label on the foil square marked with:
  1. Station
  2. Date (yymmdd) and time (24 hour military schedule) of collection
  3. Depth of collection (m)
  4. Unit code

5. Collector's initials
6. Group code (PNC, PP, NTNP, or FCHLR)
7. Container number
8. Volume of sample filtered (NOTE: When multiple filter pads are used, the volume recorded would be that used for each filter i.e. if 3 pads are used and 100 ml filtered through each pad, the filtered volume recorded should be 3 X 100 ml NOT 300 ml).

l. Place samples on ice.

- All filters may be placed together in one Ziploc bag if properly labeled.
- **Make sure no water from the cooler touches the Ziploc bags.**
- Place the 250 ml NTNP bottle in cooler and pack with ice to a level just below the bottom of the cap.

m. Completely rinse the empty filtration for next sample.

Rinse towers and bases three times with deionized water prior to seating a new filter for the next sample.

n. Empty all ½ gallon jugs and/or 2 L HDPE bottles.

Rinse all reusable sample containers with sample water prior to collecting the next sample.

A few things to remember:

- Always shake sample container thoroughly before pouring any aliquot.
- Be certain to rinse all filtering towers with DI water between samples.
- Double check each tag for completeness and clarity.
- Rinse graduated cylinders with DI water and then with sample water before processing each sample.
- Rinse 250-ml bottle with filtrate and rinse cap with sample before closing.
- Periodically the wastewater collection tank on the filtering units will require dumping. Make sure wastewater does not get into the overflow tank.
- Make sure all paper work is complete and matches the sample tags exactly.

### ***3.4 Streambank and instream sampling***

#### **3.4.1 General**

If possible, wade into the stream to collect the sample.

When sampling from the streambank, care should be taken to sample from an area that will most closely represent the entire stream.

If all samples are obtained directly from the stream, preservatives, when necessary should be added after obtaining the sample grabs.

When residual chlorine may be present, the sodium thiosulfate tablet can be added in the bottle later for bacterial samples.

### **3.4.2 Sample collection**

Collect the bacterial sample directly from the stream.

Submerge the container; neck first into the water.

Invert the bottle so the neck is upright and pointing into the water flow.

Return the filled container quickly to the surface.

Rinse the bucket with stream water 1-2 times. Fill the bucket and return to shore to fill the remaining containers.

Follow the appropriate procedures for sample preservation, labeling and storage as described in Section 2.3.

### ***3.5 Collection of samples for Chlorophyll a using syringe filtration***

Field filtration for Chlorophyll a can be done using positive pressure with a syringe. This is normally used when a few samples need to be field filtered and the vacuum apparatus would not be appropriate. Collect Chlorophyll a samples by filtering approximately 300 ml of site water (or sufficient volume to produce a visible residue on the filter) through a 150cc polypropylene syringe as follows:

1. Open the filter holder and remove the “O-ring”. Using clean forceps, place a filter on the holder with a GF/F filter. Replace the O-ring, close the filter holder and set aside.
2. Rinse the syringe by drawing a small amount of sample water up into the syringe and shaking it then discard the rinse water. Fill the syringe past the 150cc mark (150cc mark is the middle of “Y” on the syringe). Holding the syringe upward, tap on the side to eliminate as many air bubbles as possible and push the plunger until the first ridge of the plunger aligns with the middle of “Y” on the syringe.
3. Screw the syringe into the filter holder and apply gentle pressure on the plunger until the water has passed through the filter. The goal is filter 300 milliliters of sample or filter until the filter paper clogs and there is green color on the filter.

If at any time, you feel back pressure from the filter, the filter is clogged so stop the filtration and record the volume filtered on the filed data sheet.

4. To refill the syringe, carefully detach the filter assembly, fill the syringe past the 150cc mark, displace the bubbles, push the plunger to 150cc mark and continue with the filtration until the desired volume has been processed or until no water will pass through the filter with gentle pressure.
5. If at any time the filter becomes clogged due to high concentrations of suspended solids materials, stop the filtration and record the volume filtered on the field data sheet.
6. Detach the syringe from the filter assembly, pull the syringe back, shake the Magnesium Carbonate bottle, add 1 ml of saturated  $\text{MgCO}_3$  solution (10mg/L) to the syringe, reattach the syringe and apply gentle pressure to force the remaining water in the filter holder and  $\text{MgCO}_3$  onto the filter.
7. Record the final volume of the sample water filtered on the field data sheet.
8. Remove the filter holder from the syringe and open the holder. Using forceps carefully remove the filter from its holder and gently fold it in half so the pigment is inside. Should the filter tear during the removal process, discard the filter and start over again.
9. Place the filter in the center of a piece of 3 by 3 inch aluminum foil, gently fold the aluminum foil into quarters and attach the sample tag with the sample tag wire or a staple or seal the foil using the adhesive label.
10. Place the aluminum foil in a Ziploc bag and store the bag in the cooler on top of the wet ice. Make sure the opening of the bag hangs out of the cooler when the lid is lowered.
11. Rinse the filter holder apparatus thoroughly with D.I. water and ready for next sample.
12. Enter the volume filtered into CEDS along with the other field data.

### **3.6 Sediment Sampling**

#### **3.6.1 Sampling Methodology:**

Deep water sediment samples are usually collected with a Ponar grab sampler. In shallow water, sediments may be hand-sampled using a scoop. Other program's specific QAPPs may require other methods.

### **3.6.2 Sampling Location and Substrate Selection:**

When sampling from a boat, the samples should be collected away from the engine, if possible. When sampling shallow streams the samples should be collected from the submerged stream bed not from the stream bank or from the flood plain. Samples should be collected from recently deposited sediments. For all types of waters the ideal sediment contains fine particles with high organic content. Sediments with high organic content will appear dark brown or black.

Other program's specific QAPPs may have other sample sitting requirements or other sediment type requirements.

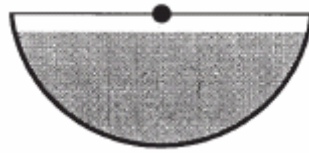
### **3.6.3 Procedure for collecting sediment samples with a 'dredge' type sampling device:**

1. Put on protective gloves before collecting the samples.
2. Prior to use, the dredge and all equipment coming in contact with the sample must have been thoroughly cleaned and properly stored to prevent contamination.
3. Prior to using the dredge at a station, rinse with site water.
4. Open the jaws of the dredge and latch it so the dredge remains open.
5. Check the knot attaching the rope to the dredge to make sure it's secure.
6. Hold the dredge over edge of the boat or bridge and lower it straight into the water. DO NOT let the dredge "freefall". It should be lowered at a rate of about one foot per second. This minimizes the effects of bow wave disturbance to surficial sediments.
7. Once the dredge hits the sediment, give the rope some slack and then pull up on the rope to force the dredge to close and take a bite of sediment from the bottom.
8. Raise the dredge at a rate of about one foot per second to minimize the effect of turbulence.
9. A successful grab is one having relatively level, intact sediment over the entire area of the dredge and a sediment depth at the center of at least 7 centimeters. (Refer to Figure 1.) The sample is examined for suitability using the following criteria:

- a. Complete closure of the dredge jaws.
  - b. No evidence of sediment washout through the dredge doors.
  - c. An even distribution of the sediment in the dredge.
  - d. Minimum disturbance of the sediment surface.
10. Drain the overlying water from the dredge being careful to prevent loss of fine sediments. Reopen the jaws of the dredge, allowing the sediment to gently slump into a clean stainless steel pan.
  11. Use a scoop to remove the top 2 to 3 cm of the sediment and place it into a second stainless steel pan. Repeat steps 3 – 10 three to five times until a sufficient volume of sediment has been accumulated. The container containing the composited sediment should remain covered with a stainless steel top or a sheet of aluminum foil during the collection of additional sediment until a sufficient volume of sediment is obtained.
  12. Remove any undesired materials (e.g. shells, leaves, stones) using clean stainless steel forceps. The sediment should be thoroughly stirred with a clean stainless steel scoop until homogeneity of texture, color and moisture is achieved. Fill the appropriate container leaving at least 1 inch of air space to prevent bursting of the sample container if it is later frozen for storage!  
Pour off any remaining overlying water in the sample.  
Label the container and place in a cooler sounding with wet ice.

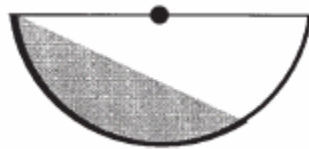
Illustrations of acceptable and unacceptable grab samples are provided in Figure 1.

Preferred Grab:



At least 7 cm of sediment with an even surface

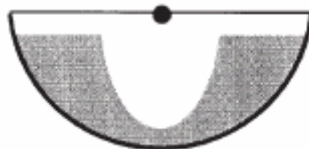
Not Preferred:



Grabs with sloping surface



Grabs with insufficient volume



Grabs with sediment washed-out



Grabs overfilled with sediment

Figure 1. Illustration of preferred and not preferred grabs

Note: The condition of sediment at each site is variable and may result in difficulty obtaining an ideal grab sample. If, after a couple of attempts, you are unable to obtain the ideal grab, use your professional judgment to obtain a suitable grab sample.

#### **3.6.4 Procedure for collecting sediment samples with a 'scoop and pan' type sampling device:**

2. Prior to use, all equipment coming in contact with the sample must have been thoroughly cleaned and properly stored to prevent contamination. The equipment should be rinsed with site water prior to sampling.
3. At the site, the sampler generally must wade into the water body to obtain a scooped sample. The sampler should approach the location from the downstream direction and must stand facing upstream, against the current, while collecting the sample.
4. Precaution must be taken not to disturb the streambed prior to sampling.
5. The sample should be scooped in an upstream direction, against the flow.
6. Scoop a sample from the sediment to a depth of 3 centimeters. Transfer the sediment into a pre-cleaned compositing tray. After the suspended sediment settles, siphon off as much water as possible. Collect three to five scoops of sediment, preferably of approximately equal volumes from separate deposits, for compositing. If sufficient sample volume was not collected with the initial scoops, collect an additional three to five scoops of sediment until the required amount of sediment is obtained.
7. Remove any undesired materials (e.g. shells, leaves, stones) using clean stainless steel forceps. The sediment should be thoroughly stirred with a clean stainless steel scoop until homogeneity of texture, color and moisture is achieved. Fill the appropriate container leaving at least 1 inch of air space to prevent bursting of the sample container if it is later frozen for storage. Pour off any remaining overlaying water in the sample. Label the container and place in a cooler with wet ice.

### **3.7 Pollution response program procedures (PREP)**

#### **3.7.1 Sampling procedures**

##### **3.7.1.1 Cyanide**

To minimize loss of cyanide due to vaporization of  $\text{CN}^-$ , the sample must be adjusted to pH 12 or more with NaOH after testing for interferences or oxidizers. The sample matrix may promote rapid loss of cyanide due to volatilization if the pH is less than 10; the sample pH must be 12 or more to hold HCN in solution and ensure representative samples.

##### **3.7.1.1.1 Total cyanide**

1. As a general rule, if residual chlorine is present in the sample, sulfide will not be present. If sulfide is present, residual chlorine will not be present.
2. If the sample contains residual chlorine, add 0.6 g. ascorbic acid per liter of sample volume.
3. Maximum holding time is 24 hours when sulfide is present.
4. To extend the holding time requirement, samples may be tested with lead acetate paper premoistened with acetic acid solution before pH adjustments in order to determine if sulfide is present.
5. If sulfide is present, it can be removed by the addition of cadmium nitrate powder until a negative spot test is obtained. The sample is then filtered.
6. Sodium hydroxide (NaOH) pellets are then added to raise the pH to 12. This can be achieved by adding a premeasured amount of NaOH to the sample - then test the sample with a pH strip and continue to add NaOH pellets until a pH of 12 is achieved.
7. Immediately after collection and pH adjustment, samples shall be cooled to 4°C in an ice chest.

##### **3.7.1.1.2 Free Cyanide**

1. To minimize CN<sup>-</sup> losses due to vaporization, the pH of the sample must be adjusted to 12 or more with NaOH.
2. This pH adjustment can be achieved by adding a premeasured amount of NaOH to the sample and then test drop by drop until a pH of 12 or more is achieved.
3. Immediately after collection and pH adjustment, samples should be cooled to 4°C in an ice chest.
4. Free cyanide samples should be exposed to light as little as possible to prevent hexacyanoferrate breakdown.

### **3.7.1.2 Sulfide**

1. Collect sample with minimum aeration in a one quart cubitainer.
2. Add 40 drops of 2N zinc acetate solution (4 drops of 2N zinc acetate solution per 100 ml sample).
3. Add NaOH pellets to raise the pH to 9.
4. Fill Bottle completely, cap container and place in an ice chest.

### **3.7.1.3 Pesticides and Herbicides**

1. Samples to be analyzed for herbicides/pesticides must be in the pH range of 5 to 9. This pH adjustment may be performed upon receipt at DCLS and may be omitted if the samples are extracted within 72 hours of collection.
2. A note should be made on the sample tag for the lab to check the pH of the sample.
3. For the analysis of aldrin, add 80 mg/l sodium thiosulfate to the water sample in the sample bottle when residual chlorine is present.
4. Immediately after collection and the addition of sodium thiosulfate, sample shall be cooled to 4°C in an ice chest.

### **3.7.1.4 Aromatic Organic Compounds**

#### ***3.7.1.4.1 Purgable Organic Compounds (Volatiles)***

1. If the sample contains residual chlorine, add 0.008% sodium thiosulfate preservative (10mg/40 ml is

sufficient for up to 5 ppm  $\text{CL}_2$ ) to the empty sample vial just prior to transport to the sampling site or at the sampling site.

2. Collect sample in a clean 500 ml stainless steel beaker. Fill two 40 ml sample vials to a positive meniscus in such a manner that no air bubbles pass through the sample as the vial is being filled. Seal the vial so that no air bubbles are entrapped in it. Turn the vial upside down to check for air bubbles. Place vials in Styrofoam packing to prevent breakage.
3. Immediately after collection, samples shall be cooled to  $4^\circ\text{C}$  in an ice chest.
4. Experimental evidence indicates that some aromatic compounds, notably benzene, toluene, and ethyl benzene are susceptible to rapid biological degradation under certain environmental conditions. Refrigeration alone may not be adequate to preserve these compounds in wastewaters for more than seven days. For this reason, a separate sample should be collected, acidified and analyzed for these aromatics.
5. A traveling blank (trip blank) must accompany all volatile organic samples. The trip blank should be prepared identically as the sample will be prepared, i.e. if 6N HCl is to be added to the sample, then acidify the blank. Add 10 mg sodium thiosulfate if chlorine residual is expected to be present. Fill a 40 ml glass vial with Teflon lined septum (acidified if sample is acidified) with analyte free water at the office. Place vial where other sampling vial will be kept throughout the whole sampling process, i.e., it travels with the sampling vial

#### ***3.7.1.4.2 Volatile aromatic hydrocarbons including Benzene, Toluene, Ethyl Benzene and Xylene (BTEX) in water samples***

- ◆ Volatile Aromatic Hydrocarbons including BTEX is the appropriate analysis for gasoline.
1. Collect sample in a clean 500 ml stainless steel beaker. Acidify sample with 6 N HCl acid to a  $\text{pH} \leq 2$ . If sample contains residual chlorine, add 10 mg sodium thiosulfate to 40 ml glass vial prior to adding sample.

2. Collect sample in replicate. Fill two vials slowly with acidified sample to a positive meniscus. Tightly secure cap. Invert to check for air bubbles. Do NOT unscrew cap on vial once cap has been secured. Resample with a new vial if air bubbles are present and discard old sample.

#### **3.7.1.5 Base/neutrals and acid extractables (Semivolatiles)**

1. If the sample contains residual chlorine, add 0.008% sodium thiosulfate (80mg/L) preservative to each of two one liter amber glass bottles and mix well.
2. Check pH of sample, if pH value falls outside the range of 6-9, adjust pH accordingly.
3. Sample must be stored in the dark.
4. Immediately after collection, samples shall be cooled to 4°C in an ice chest.

#### **3.7.1.6 Petroleum hydrocarbon identification and quantification in water samples**

1. When collecting pure petroleum product from the surface of water, fill one 40 ml glass vial having Teflon lined cap. Exclude as much water as possible from vial. It is not essential to obtain a positive meniscus. Tightly secure cap.
2. Refrigerate sample until analysis. Analyze sample within 14 days after collection.
3. The analysis of pure product will provide petroleum identification only.

#### **3.7.1.7 Total petroleum hydrocarbon (TPH) in water samples**

- TPH analysis is appropriate for kerosene, diesel, or heavier oils.
  - TPH determinations are more appropriate for soils as follow-up regulatory monitoring or when the nature of petroleum is known (i.e. tank closure).
1. Collect water samples directly in sample containers whenever possible.
  2. Collect one 1/2 pint amber glass jar with Teflon lined cap.

3. If residual chlorine is present, add 60 mg sodium thiosulfate to the 1/2 pint amber glass jar prior to adding sample.
4. Refrigerate sample until analysis. Recommended storage prior to analysis should not exceed 7 days, but federal regulations allow storage up to 14 days.

#### **3.7.1.8 Sampling when pure product is unknown**

1. Collect water samples directly in sample containers whenever possible.
2. When visual inspection of sample does not indicate noticeable pure product, but petroleum odors exist, or you are uncertain of either a noticeable product or odor, the following sample containers are needed: one 1/2 pint amber glass jar with Teflon lined cap and one 40 ml glass vial with Teflon lined septum.
3. If the sample cannot be collected directly in the sample container, one can collect the sample in a clean 500 ml stainless steel beaker. Acidify sample with 6 N HCl acid to a  $\text{pH} \leq 2$ . If sample contains residual chlorine, add 60 mg sodium thiosulfate to 1/2 pint amber glass jar and 10 mg sodium thiosulfate to 40 ml vial prior to adding sample.
4. Fill jar and vial slowly with acidified sample so that no air bubbles pass through the sample. Fill vial to a positive meniscus and immediately cap containers. Do NOT remove cap once it is secured. Invert to check for air bubbles. If air bubbles are present, fill another vial and discard old sample and container.
5. Refrigerate samples until analysis. Analyze sample within 14 days after collection.

#### **3.7.1.9 Toxicity test samples**

1. No preservatives should be added to the sample container. All air should be removed from the container.
2. The samples should be immediately iced and maintained at a temperature of 4°C.
3. If the sampler must dechlorinate the samples in the field, this must be noted on the chain of custody form with the amount of dechlorinating agent added.

4. The sample is transported directly or shipped overnight to OERS laboratory. All samples must be addressed to OERS and should contain the statement: Deliver Immediately to Laboratory.
5. A sample for toxicity tests must be used for the first time within 36 hours of collection. Exceeding this time limit voids the sample.

#### **3.7.1.10 Petroleum hydrocarbon identification, total petroleum hydrocarbons and BTEX in soil samples**

1. Collect soil sample directly into glass container for surface samples or use a clean stainless steel or Teflon scoop.
2. Fill half-pint wide mouth glass jar with Teflon lined cap. Sample should be protected from light by using an amber jar or wrapping the jar with aluminum foil.
3. Refrigerate sample during transport and storage.
4. Analyze sample within 14 days after collection

#### **3.7.1.11 Sample Handling**

1. In the ice chest, samples shall be placed upright - i.e. the neck of the sample container shall be above the level of water and ice.
2. Ship all samples to the lab as soon as practical (generally the same day as collected).

### **3.8 Collection of Trace Element Samples (Clean Metals)**

Clean metals samples are designed to quantify levels of trace elements for diagnostic programs such as TMDL or PROBMON. Because the standards for these parameters are for the dissolved component, we are looking for trace amounts (parts per billion) a “clean hands/dirty hands” approach to sampling is required.

Collection of Freshwaters, Saltwaters, and Wastewaters for the Determination of Trace Elements

#### **3.8.1 Scope**

This Standard Operating Procedure is intended to be used by the Department’s Ambient Water Quality Monitoring Staff and Permit Inspection Staff for the collection of freshwaters, saltwaters, and wastewaters with subsequent analysis by the Division of Consolidated Laboratory Services (DCLS) for dissolved and or total trace elements.

##### **3.8.1.1 Applicability**

The freshwaters appropriate for collection include all surface waters and groundwaters with a specific conductivity of approximately 1000 umhos/cm or less. Appropriate wastewaters include treated effluents with specific conductivities less than 1000 umhos/cm). Saltwaters, brackish waters, highly turbid wastewaters, i.e. landfill leachates, are also appropriate for this procedure and are collected identically as the freshwaters but require special laboratory preparation and analysis.

The protocols contained in this Standard Operating Procedure are applicable to the compounds listed in Table 1 Target Analytes, page 13.

Additionally this SOP is intended for concentration ranges of toxic trace elements (toxic metals) below approximately 200 ug/L. The 200 ug/L threshold should be applied cautiously as this is only a generalization of the effect of contamination. For example, because of well documented contamination problems with Copper and Zinc, if a final effluent has historically had copper or zinc reported in the 200 ug/L range use of this protocol may reveal that the actual concentrations are significantly lower. However if the historical numbers for cadmium, arsenic, or mercury have been greater than 200 ug/L, use of this protocol may not affect these concentrations.

For concentrations above approximately 200 ug/L, existing 40 CFR 136 procedures are adequate and contain the necessary Quality Controls (including the requirement to collect blanks) to make reliable measurements in the high ug/L range. The United States EPA Region III has prepared extensive guidance for existing and new data that falls into this higher range.<sup>[1],[2]</sup>

Table 1 lists the Method Detection Limits established for each parameter using the protocols specified in this guidance. Method Detection Limits (MDL) were measured using the procedure specified in 40 CFR 136, Appendix B.

### **3.8.2 Summary**

Ambient samples are collected in midstream by submerging a 4 liter plastic bottle, (BRIDGE BOTTLE), see Figure 1 Bridge Bottle on page 18. Using a piece of flexible tubing connected to the bridge bottle and inline with a groundwater capsule filter (TUBING KIT), the sample is transferred by peristaltic pump from the bridge bottle into a plastic SAMPLE CONTAINER, see Figure 2 Loop Sample Container on page 19 and Figure 3 Sample Container Schematics on page 20. A provision is made where the bridge bottle is substituted for a sampling wand for collecting while wading, from a boat, or anytime close contact with the sampling zone is preferred, see Figure 4 Ambient Sampling Apparatus on page 21.

Effluent samples are collected directly into a SAMPLE CONTAINER by submerging a Teflon tube into the sampling zone. Transfer is accomplished by using a piece of flexible tubing inline with the Teflon tubing and capsule filter by peristaltic pump, see Figure 4 Ambient Sampling Apparatus on page 21.

For both the river and effluent samples a provision is made for rinsing the filter and collecting a field equipment blank prior to sample collection.

The use of two field technicians is highly recommended to aid in an efficient and successful trip.

### **3.8.3 Significance and Use**

This method is primarily intended for the use in identifying and comparing dissolved trace metal concentrations to Virginia's Water Quality Standards. Water quality standards for dissolved metals are significant because the concentrations are significantly low (trace) and 2) the criteria are expressed as the dissolved metal species and not as total recoverable.

Recent findings that widely accepted field sampling methods and laboratory techniques have been responsible for significant contamination of historical data have prompted the development of this SOP. This SOP is intended to be used in situations when data on Water Quality Standards are needed or when VPDES permit discharge data are needed.

This SOP should be used when trace metal concentrations are expected to be in the sub mg/L range, typically less than 500 ug/L. At these concentrations contamination of the sample during collection and analysis is minimized or eliminated by following the SOP and taking precautions to avoid potential sources of contamination.

Contamination can occur from three main sources:

1. Improperly cleaned sample bottles and sampling equipment,
2. Improper handling of the apparatus,
3. Atmospheric debris and dust.

Bottles and equipment tested prior to field use are cleaned and tested as a quality control step at DCLS (Division of Consolidated Laboratory Service). Training on the sample collection protocols minimizes contamination introduced by improper technique. Atmospheric dust is controlled by the sampler design incorporating a closed loop collection fitting on the bridge bottle and the sample bottle, thereby minimizing the exposure of the sample to dust and debris.

When site conditions indicate a high potential for contamination, the protocol allows for the collection of field equipment blanks of ultra pure water immediately prior to using the apparatus.

### **3.8.4 Equipment Preparation and WQM Scheduling of Sample Kits**

#### **3.8.4.1 Regional Field Equipment Preparation**

The field equipment needed to collect trace metals should be stored in a plastic container to prevent dust contamination.

Prior to sampling, the peristaltic pump batteries should be charged using the cigarette adapter and charger accompanying the pump. No other battery chargers should be used as the battery system is matched to the charger. A charged battery will work continuously for about 7 hours depending on the load and ambient temperatures.

Run through your checklist to ensure that you have adequate supplies to collect the scheduled samples. Gloves are the main item you should always have in excess.

#### **3.8.4.2 Ordering Kits**

It is appropriate to maintain an adequate supply of clean metals sampling tubing and containers.

Note that Blanks are handled as separate samples and one blank should be ordered for each ambient and effluent sample.

Ambient sampling sites should be established as stations in WQM prior to sample collection and then processed using the WQM system.

Prior to sample collection, the sample containers must be ordered directly from the laboratory and the samples must be scheduled through CEDS.

ORDER SAMPLE CONTAINERS from DCLS by e-mailing Norma Roadcap (nroadcap@dgs.virginia.gov) and Charlie Morgan (chmorgan@deq.virginia.gov) with the number and type (by group codes) of samples you wish to collect, when they will be collected, and your region. PLEASE ALLOW 6 WEEKS FOR DELIVERY.

Please refer to Table 2 Parameter Group Codes on page 14 for the parameter codes to request for containers based on the sample matrix type.

Freshwater samples include the following supplies:

1. one bridge bottle,
2. one tubing kit,
3. two loop sample containers,
4. and two 100ml Mercury bottles.

Saltwater samples include the following supplies:

1. one tubing kit,
2. two loop sample containers, and
3. two 100ml Mercury bottles.

Effluent samples include the following supplies:

1. one tubing kit,
2. two loop sample containers, and
3. two 100ml Mercury bottles.

It is appropriate to store additional sample containers and kits for those situations that require rapid sample collection. The holding time for these should be a maximum of six months so replace the stored items with new kits more frequently.

### **3.8.4.3 Monthly Run Schedule**

The vast majority of these samples collected by the department are for dissolved metals. Only when you have a special study should you in addition to collecting dissolved metals should you collect total as well. You should avoid collecting only total metals as this provides very little information to the department and the cost of analysis and field resource time is very high.

Schedule samples with DCLS through the WQM system using the group codes in Table 2 Parameter Group Codes on page 14.

Please refer to Figure 6 WQM Monthly Run Schedule Parameters on page 23. Refer to the Run ID that corresponds to your type of sample whether it is an effluent (EFF), freshwater (FRESH), or saltwater (SALT). Notice that the field equipment blanks no longer have a separate group code. It is extremely important that you properly identify

the equipment blanks in the Blank/Dup field. Notice that there is not an EB for the total recoverable group code TCMETS. This is because the EB for TCMETS covers both group codes. However if you were to collect only total recoverables then it would be appropriate to have two TCMETS's one for the sample, R, and the other for the equipment blank, EB.

Because of the time and effort needed to collect metals an estimated four to five sites a day can be sampled per day.

### **3.8.5 Equipment and Supplies**

#### **3.8.5.1 Items Which Should Be Stored in Equipment Box**

The supplies are those which are needed when sampling for metals and which should be protected from dust are listed in Table 3 Equipment on page 15.

#### **3.8.5.2 Ancillary Items**

Other items which may be needed include those listed in Table 4 Ancillary Supplies on page 16.

Batteries need to be charged overnight. Prior to each sampling run check to make sure that you have enough supplies and that your portable battery is charged and functioning. The leads and fuse system on the batteries are delicate and prone to breaks and shorts. Batteries should be discharged completely and then recharged at least once every six months.

### **3.8.6 Sampling Apparatus, Bottles and Containers**

DCLS will supply all the necessary SAMPLE CONTAINERS, BRIDGE BOTTLES, and TUBING KITS based on the number and types of samples ordered through WQM.

6.1.1 When placing orders for samples try to group four to five sites. DCLS will send out coolers with kits and bottles batched for the number of samples scheduled. The same cooler can be used when returning the samples to DCLS for analysis so keep this cooler handy for bottle return.

6.1.2 The tubing kits including the filters, bridge bottles, and mercury bottles are disposable/recyclable and should be discarded after each use.

### **3.8.7 Procedure**

#### **3.8.7.1 Ambient Sample Collection Protocol For Freshwater and Saltwater Using the Bridge Bottle**

##### **7.1.1 Equipment Setup**

7.1.1.1 Locate an area where sample processing will occur. This should be an area free of falling debris and swirling dust, flat, smooth, and protected from the wind. The tailgate of a vehicle or the back of a Suburban are good locations.

7.1.1.2 Locate the equipment box and coolers containing the sample containers and kits in the area where sample processing will occur.

- 7.1.1.3 Cover the work area with a large piece of plastic film. Set out the pump and connect the battery. Switch pump on for a quick burst to check that it is working. Dial the pump speed to 5.
- 7.1.1.4 Remove a tubing kit, two loop sample containers, two mercury bottles and a bridge bottle from the cooler and place on the plastic near the pump.
- 7.1.1.5 Remove a pack of sample gloves from the storage container and place on the plastic.
- 7.1.1.6 Remove the plastic sample caddy from the storage box and place it on the sample processing area near the pump. Secure the sample bottles in the caddy.
- 7.1.2 Bridge Bottle Filling
- 7.1.2.1 Locate the sample weights for connection to the BRIDGE BOTTLE.
- 7.1.2.2 Locate the polypropylene sampling rope spool, cut a sufficient length of rope to allow for deployment.
- 7.1.2.3 Don one or two pairs of vinyl gloves using clean precautions.
- 7.1.2.4 Tie one end of the sampling rope to the five pound weight leaving approximately a 1' long end for connection to the BRIDGE BOTTLE.
- 7.1.2.5 Untie or open by tearing the top of the outer plastic bag containing the BRIDGE BOTTLE.
- 7.1.2.6 Reach into the outer bag and untie or tear the inner bag near the handle connection. Check the configuration of the tubing to ensure that proper filling will occur. Inspect the smaller vent tubing and adjust if it appears crimped due to storage. While the bottle is still in the inner bag it is acceptable to remove the top fitting to check the inner sipper tube. Adjust all fittings appropriately.
- 7.1.2.7 When the fittings have been properly secured and adjusted remove the BRIDGE BOTTLE from the inner bag and lay on the plastic film. Tie the weighted end of the rope onto the handle of the bottle leaving about 6" of line between the bottle and the weight.
- 7.1.2.8 Proceed to the sampling location with the BRIDGE BOTTLE apparatus. If appropriate carry several extra pairs of gloves to the site to facilitate bridge bottle handling.
- 7.1.2.9 When deploying from bridges with moderate to low stream velocities collect the sample upstream of the bridge by lowering the assembly into the water. Ensure that the assembly does not contact any structures or other objects as it is lowered into the water.
- 7.1.2.10 Once in the water the weight will partially submerge the BRIDGE BOTTLE, which will begin to fill. Check to insure the air release tube is above the water level and not obstructed. When the bottle is first submerged a good indication it is filling properly is a small slug of water may be expelled from the air vent tube. The bottle will fill quickly, within a few minutes, if it has been properly adjusted.
- 7.1.2.11 Problems with filling from bridges can occur when stream velocities are high. Sampling on the downstream side of bridges is acceptable to avoid the risk of losing the assembly due to the current sweeping it under a bridge or other obstruction. When stream velocities are high 7.5 pounds of weight will aid in sample collection. The added weight will cause the container to sink lower when partially filled which may submerge the vent tube. The vent tube can be extended past the bottom of the bottle to prevent filling with water when the weight is heavy or the water is rough.
- 7.1.2.12 Other problems with filling can occur when the inlet tube is clogged, the vent tube contains a slug of water or other obstruction, the vent tube is below the surface of

the water, the weight is not positioned close enough to the bottle, or the vent tube or inlet tube has become disconnected from the bottle.

7.1.2.13 When the BRIDGE BOTTLE is approximately 1/2 to 2/3 full, retrieve the bottle and return to the sample processing area. It is acceptable to allow the bridge bottle to sink completely below the surface as long as the inlet tube does not contact the bottom. Ensure that the assembly does not contact any structures or other objects as it is retrieved.

7.1.2.14 When deploying while wading or from a small craft the BRIDGE BOTTLE can be submerged by hand without the weights.

7.1.2.15 When the water level at the sample site is very shallow it may be difficult to submerge the BRIDGE BOTTLE deep enough to begin siphoning. The alternative is to use the effluent sample configuration where the stream sample is pumped directly into the loop sample container. Sampling in this manner requires the pump assembly to be transported to the site. This is best accomplished by attaching the pump assembly to a backpack.

7.1.2.16 Once the BRIDGE BOTTLE has been brought back to the sample processing area set it next to the pump and remove the weight. With the inlet and vent tubing properly configured the BRIDGE BOTTLE can remain on the plastic outside of a bag without any danger of atmospheric contamination.

#### 7.1.3 Ambient Dissolved Grab Blanks

7.1.3.1 Refer to Figure 4 Ambient Sampling Apparatus on page 21 for the schematic of the field sampling equipment used to process blanks and samples.

7.1.3.2 Determine which tech will be clean hands and which will be dirty hands.

7.1.3.3 Dirty hands and clean hands don one or two pairs of vinyl gloves. Dirty hands opens the sample bottles outer plastic bag, clean hands opens the inner plastic bag. At this point there should be two loop bottles and two mercury bottles available to clean hands.

7.1.3.4 Dirty hands opens the grab kit's outer plastic bag, clean hands opens the inner plastic bag and removes the tubing assembly.

7.1.3.5 Clean hands disconnects one side of the sample loop on the first sample container. Clean hands connects the end of the tubing kit opposite the filter to the opened sample container. Remember the sample container is full of clean water from the lab.

7.1.3.6 Dirty hands connects the peristaltic tubing at approximately the mid-point of the length to the field pump, clean hands inverts the sample container, and dirty hands switches on the pump.

7.1.3.7 Process the entire contents, 1000mls, of the sample container through the tubing and filter apparatus at a flow rate of 500mls/min (pump setting of 5). At the beginning of the sample processing orient the filter cartridge with the flow arrow pointing up. This will insure proper wetting of the filter.

7.1.3.8 When the last continuous stream of water enters the filter dirty hands switches off the pump. The filter must not be allowed to go dry. This is a change from the previous SOP and is necessary because of problems with excessive back pressure causing tubing separation from the filter.

7.1.3.9 This step is a rinse of the filter, which cleans and conditions the media. The rinse can be pumped directly to waste, as this is ultra pure water.

7.1.3.10 Clean hands disconnects the pump tubing from the empty loop bottle and reconnects this same end to the second loop bottle containing blank water. Remember that this second bottle is full of clean water from the lab. Clean hands inverts the container, dirty hands switches on the pump. Process the blank water from the loop bottle until approximately 125mls have been expelled from the filter. Dirty hands switches off the pump.

7.1.3.11 This step removes the last trace of conditioning water left in the filter. Clean hands opens the first mercury container and discards the water. Clean hands holds the outlet of the capsule filter just above the open mouth of the mercury bottle. Fill the mercury bottle to overflowing and cap. Make sure there are no air bubbles in the bottle that are larger than a pea. Connect the capsule filter outlet to the empty loop container via the sample loop tubing. Process the remaining contents, approximately 900mls, of the sample container through the tubing and filter apparatus into the first sample container taking care not to pump the filter dry.

7.1.3.12 Clean hands disconnects the outlet tubing from the blank sample container and immediately reconnects the loop tubing on the top of the blank bottle.

7.1.3.13 The field blanks collected in this manner are comprehensive blanks because they are collected in the same equipment as the sample and are processed like the sample through all steps of the protocol. This is the most important check of contamination in the protocol.

#### 7.1.4 Ambient Dissolved Grab

7.1.4.1 Clean hands immediately (immediately means the sooner the switch is made the less likely contamination can adhere to the end of an open tube, immediately means less than one minute) disconnects the vent tubing from the BRIDGE BOTTLE and then connects the inlet side of the pump tubing in place of the vent tubing.

7.1.4.2 Dirty hands switches on the pump. Process the sample water from the BRIDGE BOTTLE until approximately 125mls have been expelled from the filter. Dirty hands switches off the pump.

7.1.4.3 Clean hands opens the second mercury container and discards the water. Clean hands holds the outlet of the capsule filter just above the open mouth of the mercury bottle. Fill the mercury bottle to overflowing and cap. Make sure there are no air bubbles in the bottle that are larger than a pea.

7.1.4.4 Clean hands unscrews the cap of the second loop sample container and discards the small amount of water remaining in the container. Clean hands returns the top to the container and then connects the capsule filter outlet to the second empty loop container via the sample loop tubing. Process the sample into the loop container until the container is full. Dirty hands switches off the pump. It is acceptable to fill the sample container to overflowing, however avoid filtering more than 1000 mls through the filter.

7.1.4.5 Clean hands disconnects the outlet tubing from the sample container and immediately reconnects the loop tubing back in place to seal the sample bottle.

7.1.4.6 Clean hands holds the blank loop container in a manner to allow dirty hands to place the WQM label directly on the midsection of the bottle. The mercury container also has the WQM label placed on the midsection in the same manner as above. The mercury blank container is then placed into the inner bag of the blank loop container seals the inner bag. Dirty hands seals the outer bag.

7.1.4.7 This process is repeated for the sample bottle and mercury sample.

- 7.1.4.8 The blanks and samples should be immediately placed on ice in a separate sample cooler containing only clean metal containers. This is to prevent the wire sample tags from contaminating the clean samples.
- 7.1.4.9 It is no longer necessary to record the ultra bottle numbers but it is important that the WQM labels are used to correctly identify the samples and blanks. The container numbers chosen in WQM do not need to correspond to the ultra bottle numbers.
- 7.1.4.10 Rinse the rope and weights with ambient water to remove any visible dirt, place inside a plastic bag, and store in the storage container. Rope may be reused several times if rinsed frequently.[\[RES1\]](#)
- 7.1.5 Ambient Total Recoverable Grabs
- 7.1.5.1 If total recoverable samples are to be collected in conjunction with dissolved samples, during all phases of sample collection of the dissolved samples the BRIDGE BOTTLE must be shaken to ensure proper mixing of suspended solids. Additionally during the total recoverable sample collection the BRIDGE BOTTLE must continue to be shaken.
- 7.1.5.2 When collecting for total recoverable samples after first collecting for dissolved samples the tubing used to collect the dissolved fractions must be protected after the last dissolved samples are collected.
- 7.1.5.3 Clean hands removes the capsule filter from the tubing. Clean hands opens the third mercury container and the third total recoverable loop bottle and discards the water. The loop bottle cap should be replaced immediately after discarding the water. Dirty hands switches on the pump and clean hands fill the mercury bottle to overflowing and then caps as described above. The tubing is then connected to the total recoverable loop container and it is also filled until full. Clean hands immediately reconnects the loop tubing to seal the container.
- 7.1.5.4 Clean hands holds the total recoverable loop container in a manner to allow dirty hands to place the WQM label directly on the midsection of the bottle. The mercury container also has a the WQM label placed on the midsection in the same manner as above. Clean hands places the mercury total recoverable container into the inner bag of the total recoverable loop container seals the inner bag. Dirty hands seals the outer bag.
- 7.1.5.5 The blanks and samples should be immediately placed on ice in a sample cooler.
- 7.1.6 Other Parameters
- 7.1.6.1 The clean protocol is complete at this step and field parameters can now be taken from the remaining water in the BRIDGE BOTTLE. Recommended field parameters include: pH, Conductivity, Temperature, and Dissolved Oxygen. Additional laboratory samples for the solid series and total organic carbon should be collected and identified by the group codes: SOLID and TOC.
- 7.1.6.2 Rinse the rope and weights with ambient water to remove any visible dirt, place inside a plastic bag, and store in the storage container. Rope may be reused several times if rinsed frequently.[\[RES2\]](#)

### **3.8.7.2 Effluent Sample Collection Protocol**

- 7.2.1 Equipment Setup
- 7.2.1.1 Locate an area near the final effluent sampling location where sample processing will occur. This should be an area free of falling debris and swirling dust, flat, smooth,

and protected from the wind. The tailgate of a vehicle or the back of a Suburban are good locations.

7.2.1.2 Locate the equipment box and coolers containing the sample containers and kits in the area where sample processing will occur.

7.2.1.3 Cover the work area with a large pick of plastic film. Set out the pump and connect the battery. Switch pump on for a quick burst to check that it is working. Dial the pump speed to 5.

7.2.1.4 Remove a tubing kit and two sample containers from the cooler and place on the plastic near the pump.

7.2.1.5 Remove a pack of sample gloves from the storage container and place on the plastic. Refer to, for the schematic of the field sampling equipment used to collect treatment plant grab samples.

7.2.1.6 Remove the plastic sample caddy from the storage box and place it on the sample processing area near the pump.

7.2.1.7 Locate the sample wand used for positioning the Teflon sample tubing in the effluent.

7.2.2 Effluent Dissolved and/or Total Recoverable Grab Blanks and Samples

7.2.2.1 Refer to Figure 5 Effluent Sampling Apparatus on page 22 for the schematic of the field sampling equipment used to process blanks and samples.

7.2.2.2 The effluent grab blanks and samples are collected in exactly the same manner as the ambient grab blanks and samples. Please refer to sections 7.1.3, 7.1.4, and 7.1.5.

7.2.2.3 Beginning with section 7.1.4 instead of collecting from a bridge bottle it is preferred to use a PVC sample wand equipped with a special notch to hold the Teflon tubing.

7.2.2.4 REFERENCE PICTURE OF NOTCH

7.2.2.5 Clean hands presents a section of the Teflon tubing just past the inlet to dirty hands who then attaches the tubing to the sample wand.

7.2.2.6 The entire assembly: sample caddy containing the empty sample container, sample tubing, pump/battery, and sample wand are transported to the effluent sampling location.

7.2.2.7 Dirty hands places the sample wand into the collection zone taking precaution not to touch the tip of the sampling tube on any items. Once the sample tube is located in the effluent, take precautions not to let the tip contact anything but water.

7.2.2.8 At this point refer to 7.1.4.2 on how to process samples. The procedure is complete once you have reached step 7.1.5.5.

### **3.8.8 Sample labeling**

When the sample run is scheduled, the labels should be printed from the CEDS. Make sure to use the label has good quality glue on it (i.e. Avery). Labels shall be filled out with date and time and affixed to bottles prior to bottles getting wet. Do not stick the label outside the plastic bag.

### **3.8.9 Sample Shipping**

#### **3.8.9.1 Supplies and Materials**

- 9.1.1 Shipping cooler which is insulated, with a polyethylene lid. A 28 quart cooler is sufficient size to hold sample bottles, wet ice packs, and protective material. It has a detachable lid, no drain hole, and is easy to clean. It is a convenient size and shape for handling, stacking, and storing as it not too heavy when fully packed.
- 9.1.2 Liner Bags which are 30 gallon plastic trash bags with a dimension of 30" X 36" X 1mil.
- 9.1.3 Plastic bubble wrap packing material with 1/2" bubbles in 12" X 16" sheets used for wrapping the 1 liter sample containers. The material is available in various configurations with the 1' wide roll suitable for the loop containers.
- 9.1.4 Rubber bands size 33 or large enough to secure the bubble wrap around 1 liter containers packed in two Ziplocs.
- 9.1.5 Ice bags which are heavy duty 1 gallon Ziploc bags.
- 9.1.6 Wet ice cubes.
- 9.1.7 1 Liter plastic scoop.
- 9.1.8 Strapping tape, 1" filament type.
- 9.1.9 Duct tape, 2" utility type.
- 9.1.10 Sealing tape, 3" clear acrylic adhesive holds well in cold temperatures, stays transparent for long periods, and is suitable for sealing ice bags and protective labels on bottles and coolers.
- 9.1.11 Packing list envelopes, clear plastic self adhesive type. Overnight services are a good source.
- 9.1.12 Address Labels, specific to the carrier.

#### **3.8.9.2 Sample Packaging**

- 9.2.1 Immediately following sample collection place sample bottles in storage cooler with bagged wet ice and chill prior to packing shipping coolers.
- 9.2.2 Insert two trash bags into the cooler for double lining.
- 9.2.3 Just prior to packing the sample coolers, prepare ice packs with fresh ice cubes. Fill each ice bag with approximately 1.5 pounds of ice. A one liter scoop is a good amount. Seal each Ziploc bag expelling as much air as possible and seal. If shipping conditions are expected to be severe, i.e. rough treatment, the ice bags can be further secured with clear sealing tape.
- 9.2.4 Place the chilled sample containers upright into the lined cooler and surround with ice packs. The sample containers and ice should be tightly packed. When the cooler is properly packed there will be no extra space left in the cooler.
- 9.2.5 The number of containers that can be packed into a cooler along with a sufficient amount of ice will obviously depend on the cooler dimensions and the ratio of ice to containers. Generally five 1 liter plastic bottles with bubble wrap and seven ice packs will fit into a 28 quart cooler. The weight of the cooler should not exceed 70 pounds.
- 9.2.6 Seal each liner bag by twisting the top of the bag and tying in a knot.
- 9.2.7 If appropriate attach a packing list envelope to the underside of the shipping cooler lid, insert the appropriate sample documentation (e.g. chain of custody form, field data sheets, or special lab instructions) and seal the envelope for protection.

- 9.2.8 Close the lid, seal horizontal joints with duct tape, and secure with strapping tape.  
9.2.9 Attach address label to side of cooler and protect with clear sealing tape.

### **3.8.9.3 Sample Transportation**

- 9.3.1 Samples shipped by common carrier must comply with applicable Department of Transportation Hazardous Materials Regulations, 40 CFR Part 172. The person offering such material for transportation is responsible for ensuring such compliance. See 40 CFR Part 136 Table II for guidance on applicability of preserved environmental samples.  
9.3.2 Ship samples on the day of collection and use a reliable courier service for priority or next day delivery.  
9.3.3 A large amount of effort is required to sample four to five sites and a large amount of work preparing the sample equipment and containers has taken place. Four samples represents \$1000.00 in equipment preparation and analytical costs so coordinate sample shipment closely with DCLS and continue follow-up communication until delivery is confirmed and condition of samples upon receipt is verified.  
9.3.4 The above sample packaging and transportation are provided for those samples that are to be shipped long distances generally interstate and are intended for worst case shipping conditions.  
9.3.5 For those samples shipped via our standard DCLS courier service no special precautions beyond normal shipping procedures are required.

### **3.8.9.4 Quality Control**

- 9.4.1 The protocols in this SOP are designed to include all the necessary Quality Control steps needed to produce reliable accurate data.  
9.4.2 Table 5 Quality Control Recommendations for Trace Metals Sample Collection on page 17 lists the critical control points of the sampling protocol. These control points are the minimum steps required for the collection of samples. When field contamination is detected additional blanks and other quality control samples are absolutely necessary to identify and correct the problem.  
9.4.3 Field equipment blanks (identified as EB with a depth of 0.0 in WQM) should be collected with every sample including the mercury blank. If total recoverable samples are also collected the dissolved equipment blank will be representative of the total recoverable sample. If only total recoverable samples are collected then a field equipment blank is required.  
9.4.4 For effluent sites blank samples must be collected prior to each and all trace metal samples.  
9.4.5 If ambient site conditions indicate potential problems then it would be wise to collect additional samples. Some site conditions which would warrant blanks prior to sample collection are:
1. road construction producing visible dust,
  2. any operation causing visible dust emissions,
  3. high total suspended solids conditions instream,
  4. recent deicing of bridges,
  5. high traffic volume on bridge and,
  6. heavy rain events during sampling.

Periodically, at a frequency of greater than 10%, field duplicates should be collected. Field duplicates for ambient sample collection involve processing an additional blank and sample from the BRIDGE BOTTLE.

Field duplicates for effluent sample collection involve processing an additional blank and sample in series from the effluent and may produce results variable results due to the component of temporal variability.

### **3.8.9.5 Referenced Documents**

The methods and research articles used to develop the field sampling equipment are:

1. Benolt, Gaboury, Clean Technique Measurement of Pb, Ag, and Cd in Freshwater: A Redefinition of Metal Pollution, Environ. Sci. Technol., Vol. 28, No. 11, 1994.
2. Horowitz, A.J. et. al., The Effect of Membrane Filtration Artifacts on dissolved Trace Element Concentrations, Wat. Res. Vol. 26, No. 6, pp. 753-763, 1992.
3. Horowitz, Arthur J., et.al., On the Problems Associated with Using Filtration to Define Trace Element Concentrations in Natural Water Samples, U.S. Geological Survey.
4. Martin, Gary R., et.al., ), A Comparison of Surface-grab and Cross Sectionally Integrated Stream-water-quality Sampling Methods, Water Environment Research, Volume 64, 866 (1992).
5. Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels, EPA 821-R-95-034, April 1995.
6. Geological Survey Protocol for the Collection and Processing of Surface-Water Samples for the Subsequent Determination of Inorganic Constituents in Filtered Water. United States Geological Survey, Open-File Report 94-539.

These methods provide an excellent source of information on the proper handling of sampling equipment and the collection of samples for the analysis of trace metals. The techniques used to collect contamination free environmental samples are involved and require a significant understanding of the principles of trace analysis. It is beyond the scope of this SOP to provide all the details that would be necessary to allow an inexperienced field team to collect trace metal samples. These protocols should be used by persons experienced in the collection of environmental samples for trace analysis and who are familiar with the sources and magnitude of ambient contamination.

Table 1 Target Analytes

Parameter	CAS number	Method Detection Limits, µg/L					
		ICPMS USN FRESHWATER	ICPMS USN SALTWATER	ICPMS USN TR FRESHWATER	ICPMS USN TR SALTWATER	ICPMS	ICP AES USN
<b>Aluminium</b>	7429-90-5			0.04		0.37	
<b>Antimony</b>	7440-36-0	0.05		0.03		0.33	
<b>Arsenic</b>	7440-38-2	0.07		0.03		0.24	5.37
<b>Barium</b>	7440-39-3						
<b>Beryllium</b>	7440-41-7						
<b>Cadmium</b>	7440-43-8	0.05		0.04		1.72	2.37
<b>Calcium</b>	7440-70-2						0.08
<b>Chromium</b>	7440-47-3	0.02		0.04			2.27
<b>Copper</b>	7440-50-8	0.02		0.06		0.67	4.98
<b>Iron</b>	7439-89-6						2.30
<b>Lead</b>	7439-92-1	0.17		0.03		0.28	
<b>Magnesium</b>	7439-95-4						0.00
<b>Manganese</b>	7439-96-5	0.02		0.03		1.32	0.58
<b>Mercury</b>	7439-97-6					0.12	
<b>Nickel</b>	7440-02-0	0.04		0.02		0.39	1.71
<b>Selenium</b>	7782-49-2			0.06		0.77	
<b>Silver</b>	7440-22-4	0.19		0.03		0.15	
<b>Thallium</b>	7440-28-0						
<b>Zinc</b>	7440-66-6	0.26		0.03		2.18	1.95

ICPMS USN inductively coupled plasma mass spectrometry sample introduced by ultrasonic nebulization

ICPMS USNTR inductively coupled plasma mass spectrometry sample introduced by ultrasonic nebulization total recoverable

ICPMS inductively coupled plasma mass spectrometry

ICP AES USN inductively coupled plasma atomic emission spectrometry sample introduction by ultrasonic nebulization

Atomic Fluor atomic fluorescence spectrometry

Table 2 Parameter Group Codes

FRESHWATER	
DCMET	Dissolved clean metals in freshwater
TCMET	Total clean metals in freshwater

SALT WATER	
DCMETS	Dissolved clean metals in saltwater
TCMETS	Total clean metals in saltwater

EFFLUENT	
CMEFF	Dissolved clean metals in effluents
TCMEFF	Total clean metals in effluents

N.B. All of the above group codes include mercury and the associated extra container. For mercury only please see the group codes below.

MERCURY ONLY	
DCHG	Dissolved mercury in freshwater
TCHG	Total mercury in freshwater

Table 3 Equipment

	Item	Supplier	Catalog Number
<b>1</b>	peristaltic pump unit	Cole-Parmer	H-07533-40
<b>2</b>	quick release pump head	Cole-Parmer	H-07518-60
<b>3</b>	cigarette lighter adapter cable	Cole-Parmer	H-07573-02
<b>4</b>	portable battery pack	Cole-Parmer	H-03276-50
<b>5</b>	powder free vinyl gloves	Fisher Scientific	11-387-3
<b>6</b>	clear colorless polyethylene drop cloth	hardware store	4 to 6 mil
<b>7</b>	preprinted laserjet waterproof labels	Avery	5163
<b>8</b>	indelible markers	Sharpies	office supply
<b>9</b>	bridge bottle	DCLS	N/A
<b>10</b>	bridge bottle tubing kit	DCLS	N/A
<b>11</b>	teflon tubing kit	DCLS	N/A
<b>12</b>	samples bottles	DCLS	N/A
<b>13</b>	one gallon ziplock bags	grocery store	N/A
<b>14</b>	two gallon ziplock bags	grocery store	N/A
<b>15</b>	bridge bottle weights	sporting goods store	N/A
<b>16</b>	white polypropylene line	hardware store	N/A

Table 4 Ancillary Supplies

	Item	Supplier	Catalog Number
<b>1</b>	plastic bubble wrap	consolidated plastics	87600LG
<b>2</b>	rubber bands	office supply store	large
<b>3</b>	ice	grocery store	N/A
<b>4</b>	duct tape	hardware store	N/A
<b>5</b>	knife or cutters	hardware store	N/A
<b>6</b>	fuses for pump and battery	hardware store	N/A

Table 5 Quality Control Recommendations for Trace Metals Sample Collection

**QUALITY CONTROL RECOMMENDATIONS FOR TRACE METALS SAMPLE COLLECTION**

SAMPLING REQUIREMENTS	CRITERIA	FREQUENCY
Type of method	Performed based by demonstration of no detectable contamination of target analytes or interferences in samples or blanks. Method 1669 and the sampling apparatus and techniques used by the DEQ are recommended for sample collection.	Demonstration contamination free samples and blanks everytime a variation is made to the method
Media Type	Freshwater and treated final effluent wastewater for dissolved and total recoverable metals.	NA
Training	Sample collection by only thoroughly trained personnel. Personnel must demonstrate proficiency in collecting contaminant free blanks and samples.	Train a minimum of one time prior any sample collection. Stop and provide additional training if field QC demonstrates problems until the criteria is achieved.
Filtration	0.45 um Capsule filter with nominal surface area of 600 cm <sup>2</sup> . Maximum sample volume 1000 ml through single use filter.	Onsite at time of collection or within one hour for composite samples after the sample sequence is complete.
Sample containers	no detectable target analytes above MDL.	minimum of 1% of containers checked by the laboratory per batch after intial demonstration of acceptable blank QC.
Sampling equipment	no detectable target analytes above MDL.	minimum of 1% of equipment checked by the laboratory per batch after intial demonstration of acceptable blank QC.
Comprehensive grab field blank	blanks must be < 10% sample concentration or if sample is < MDL field blank contamination is OK.	Process one with every sample collected. When duplicate samples are collected only one blank is necessary.
Comprehensive composite field blank	Blanks must be < 10% sample concentration or if sample is < MDL field blank contamination is OK.	Process one per site for every ten samples. When 10% frequency rule is applied blanks are to be collected with the first sample. Process field blank every time equipment is field cleaned to be reused between sites or sample events.
Field duplicate	Statistically equivalent to the RPD of the matrix spike and matrix spike duplicates for quantifiable concentrations	Process one per site for every ten samples.
Preservation	Samples must be iced in the field. Composite samples must be iced during collection. pH < 2 within 72 hours of collection and samples must remain in original containers for a minimum of 18 hours prior to digestion or analysis.	All samples must be acid preserved in the field or laboratory with ultra pure HNO <sub>3</sub> to pH < 2. Samples should be iced in field immediately after collecting.
Documentation	Sampling activities must be documented on paper or by computerized sample tracking.	Documentation must be done per sample per site.

Figure 1 Bridge Bottle



Figure 2 Loop Sample Container and Mercury Container



Figure 3 Sample Container Schematics

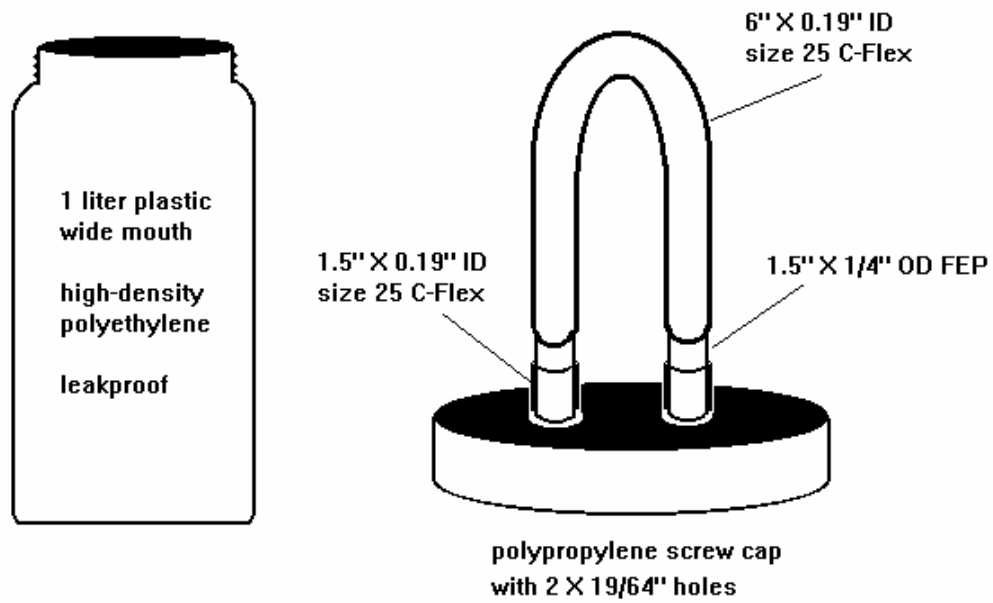


Figure 4 Ambient Sampling Apparatus

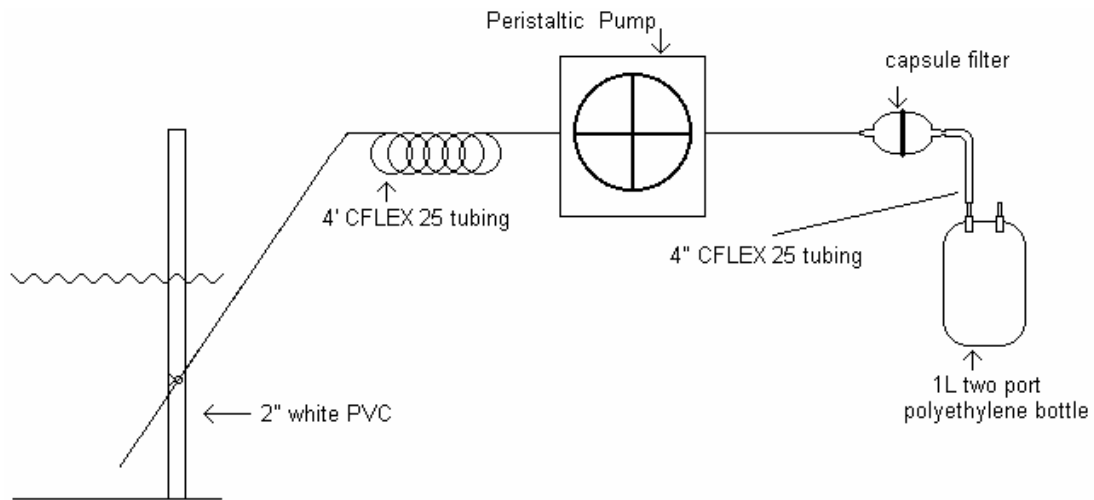


Figure 5 Effluent Sampling Apparatus

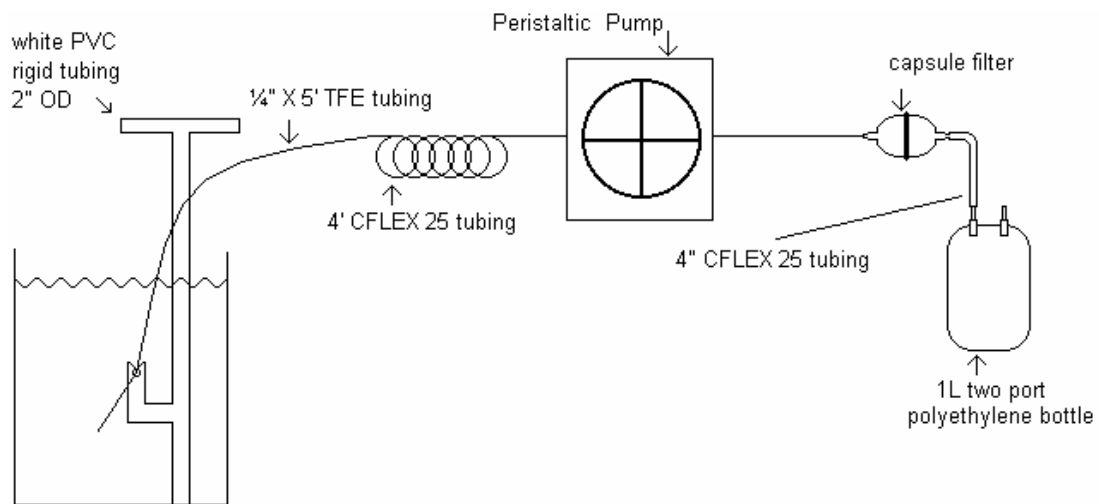


Figure 6 WQM Monthly Run Schedule Parameters

Virginia Department of Environmental Quality - [Monthly Runs Schedule]

Action Edit Block Field Record Query Window Help

Print Field Sheet Monthly Runs Schedule Get YRS Data Get Multiple YRS

Run ID	Station ID	Survey Pgm	Depth Desc	Depth	% FRB	Blank / Dup	Cont ID	Lab Proc Code	Special Studies #	Parameter Group Cd	Date Sample Collected
EFF	VA60364001	QA	S	0	50	EB	1			CMEFF	11/05/2000
EFF	VA60364001	FI	S	.3	50	R	2			CMEFF	11/05/2000
EFF	VA60364001	FI	S	.3	50	R	3			TCMEFF	11/05/2000
FRESH	2-JMS111.17	QA	S	0	50	EB	1			DCMET	11/05/2000
FRESH	2-JMS111.17	AQ	S	.3	50	R	2			DCMET	11/05/2000
SALT	2-SBE001.53	QA	S	0	50	EB	1			DCMETS	11/05/2000
SALT	2-SBE001.53	AQ	S	.3	50	R	2			DCMETS	11/05/2000
SALT	2-SBE001.53	AQ	S	.3	50	R	3			TCMETS	11/05/2000
			S								

FRM-40400: Transaction complete: 6 records applied and saved.  
Count: \*8

## 11. Quick Reference Guide

### 11.1 Ambient Sample Collection Quick Reference

- 11.1.1 Tie the 5 pound weight to the bridge bottle.
- 11.1.2 Collect the sample using the bridge bottle.
- 11.1.3 Untie the 5 pound weight.
- 11.1.4 Connect the tube to the first loop container.
- 11.1.5 Rinse the filter with the contents of the container.
- 11.1.6 Remove the tube from the empty bottle and place on the second loop container.
- 11.1.7 Pump 125mls of water to waste through the filter to purge previous sample.
- 11.1.8 Fill the mercury blank and seal.
- 11.1.9 Connect the filter to the empty first loop container.
- 11.1.10 Pump out of the second loop container into the first without letting the filter go dry.
- 11.1.11 Seal the blank loop container.
- 11.1.12 Remove the tube from the now empty second loop container and reconnect the tube to the bridge bottle vent tube.
- 11.1.13 Pump 125mls of water to waste through the filter to purge previous sample.

- 11.1.14 Collect the mercury sample.
- 11.1.15 Unscrew the lid of the second loop container and discard the water and replace the lid.
- 11.1.16 Connect the filter to the second loop container and fill.
- 11.1.17 Seal the sample containers.
- 11.1.18 Remove the filter and collect the total recoverables.
- 11.1.19 Collect field parameters.
- 11.1.20 Pack in ice and transport.

## 11.2 *Effluent Sample Collection Quick Reference*

- 11.2.1 Connect the tube to the first loop container.
- 11.2.2 Rinse the filter with the contents of the container.
- 11.2.3 Remove the tube from the empty bottle and place on the second loop container.
- 11.2.4 Pump 125mls of water to waste through the filter to purge previous sample.
- 11.2.5 Fill the mercury blank and seal.
- 11.2.6 Connect the filter to the empty first loop container.
- 11.2.7 Pump out of the second loop container into the first without letting the filter go dry.
- 11.2.8 Seal the blank loop container.
- 11.2.9 Remove the tube from the now empty second loop container and connect the tube to the sample wand.
- 11.2.10 Pump 125mls of water to waste through the filter to purge previous sample.
- 11.2.11 Collect the mercury sample.
- 11.2.12 Unscrew the lid of the second loop container and discard the water and replace the lid.
- 11.2.13 Connect the filter to the second loop container and fill.
- 11.2.14 Seal the sample containers.
- 11.2.15 Remove the filter and collect the total recoverables.
- 11.2.16 Collect field parameters.
- 11.2.17 Pack in ice and transport.

### 11.3 *Ambient Sample Collection Without the Bridge Bottle Quick Reference*

- 11.3.1 Connect the tube to the first loop container.
- 11.3.2 Rinse the filter with the contents of the container.
- 11.3.3 Remove the tube from the empty bottle and place on the second loop container.
- 11.3.4 Pump 125mls of water to waste through the filter to purge previous sample.
- 11.3.5 Fill the mercury blank and seal.
- 11.3.6 Connect the filter to the empty first loop container.
- 11.3.7 Pump out of the second loop container into the first without letting the filter go dry.
- 11.3.8 Seal the blank loop container.
- 11.3.9 Remove the tube from the now empty second loop container and connect the tube to the sample wand.
- 11.3.10 Pump 125mls of water to waste through the filter to purge previous sample.
- 11.3.11 Collect the mercury sample.
- 11.3.12 Unscrew the lid of the second loop container and discard the water and replace the lid.
- 11.3.13 Connect the filter to the second loop container and fill.
- 11.3.14 Seal the sample containers.
- 11.3.15 Remove the filter and collect the total recoverables.
- 11.3.16 Collect field parameters.
- 11.3.17 Pack in ice and transport.

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<sup>[1]</sup> NPDES Self-Monitoring Data and Data Audit Inspections (DAIs), United States Environmental Protection Agency Region III, Central Regional Laboratory, Fall 1994.

<sup>[2]</sup> Metals' Data Position Paper, United States Environmental Protection Agency Region III, Rev 5.0, May 1, 1995.

<sup>[3]</sup> Tom Fieldsend of Sample Control Center, Operated by DynCorp Environmental for USEPAs Engineering and Analysis Division provided the protocol for sample shipping.

### **3.9 Chain of Custody Procedures**

Chain of Custody Procedures are only utilized when samples are required to be legally defensible in court such as in the case of Incidence Response samples.

#### Implementing the Chain of Custody Procedures

The Chain of Custody Record (COCR) shall provide documentation of everyone who has custody of the samples. The sample collector starts the COCR when the samples are collected. The COCR travels with the samples that are listed on the COCR. The COCR must contain the written signature of everyone that has custody of the samples and must document the relinquishment and receipt of the samples between sample custodians.

#### Transferring COC of samples from person to person

When custody of the samples changes, i.e. when samples are transferred from one person to another, the Custody Record must show the samples being relinquished by one person and received by another in the presence of each other. The custody of the samples and the responsibility of maintaining sample integrity are transferred during this process. The transfer process is documented on the bottom of the Chain of Custody Record form.

#### Transferring COC of samples from person to via courier

This transfer is the same as above except that the transfer is not face to face. Both the collector and receiver document the integrity of the shipping container and the samples therein. The actual sample transfer is via courier in a tamper-proof shipping container.

#### Preparing the COCR Form

The COCR form may be prepared using one of two methods, CEDS or manually. The preferred method is to use the CEDS system and the COCR form printed from information entered into the CEDS system. When using lab sheets, a multiple-part preprinted carbonless form is used. The COCR does not take the place of a lab sheet or CEDS data shipment. Consideration must be taken of the number of samples being shipped, as **a separate form must be completed for each cooler shipped**. Care must be taken to ensure that the information on the form concerning the samples exactly matches that found on the samples. Samples must be rejected if they do not match the COCR form.

#### Sample Priority

Using the COCR does not in itself indicate the samples are priority. The priority number should be recorded on the COCR in the space where the 24-hour contact information is located. When using CEDS, this information is also captured in the field data screen and shipped to lab. When using lab sheets, each lab sheet must have the priority code

entered. Advance notice of priority samples, or samples being delivered on a weekend, should be given the lab by contacting persons on the contact list. Only high priority samples or samples with short holding times should be shipped to the lab for weekend delivery.

#### SHIPPING SEAL NUMBER

This is number of the wire seal provided by lab that will be used to seal the individual coolers. All coolers not delivered in person to DCLS must have a shipping seal in place with the shipping seal number recorded on the COCR. The seal number is unique and entering it on the COCR makes that record unique. When the cooler is received by lab they will compare the number of the unbroken seal on the cooler with the seal number that is recorded on the COCR.

#### FORM NUMBER

The multi-part forms will have a unique form number in the top right hand portion of the page. This number will be used to identify the form from all others when no shipping seal number is used.

#### SAMPLERS

The person who collects the samples or is present when the samples are collected and labeled and takes initial custody of the samples signs the COCR in this area.

#### CASE NO. OR PC NO. OR VPDES NO. OR OTHER

This area is used to record the reference number for the sampling event. The number is program specific. Program protocols should be followed when entering this number. When using CEDS this reference number is referred to as the RUN ID.

#### LAT. & LONG (optional)

The latitude and longitude may be entered at the top of the page if known. This is used to identify the location of the sampling event. If more than one site is sampled during the sampling event, a lat/long must be entered for each station and lat/long space at the top of the page should be left empty.

#### REGION OR UNIT and ADDRESS

Enter the name of the region or central office unit responsible for collecting the samples and the address of the region or unit. This address may be used when returning certificates of analysis.

#### PHONE & FAX NUMBERS AND E-MAIL

Enter this contact information for the collector. This information will be used to contact the collector if questions arise concerning the samples or analysis.

#### 24-HOUR CONTACT INFORMATION

Enter the sample priority in this area. If the samples have a high priority (1), enter any and all information that can be used 24-hours a day to confer about sample analysis and results. Examples of information are; home, work, pager and cell phone numbers as well as e-mail addresses.

#### STATION ID

This is the brief description of the station at which the samples listed (on the same line) were collected. Limit the description to information necessary for you to uniquely identify the station from all others collected. This information must match the information on the sample tags and in the field log.

#### DATE/TIME

This is the date and time at which the samples were collected. The date is in the form MMDDYYYY and time is recorded in military time.

#### BASIC STATION DESCRIPTION OR CONTAINER TYPE (optional)

This space is used for additional station description information if necessary. For situations where pre-cleaned containers are used, the container description information may be entered here.

#### COMP./GRAB (optional)

This space may be used to identify samples other than routine grab samples. In the case of composite samples, the number of samples or time frame of the composite should be entered. If a horizontal or vertically integrated sample is collected, the information may be entered in the station description or under "FIELD OBSERVATIONS".

#### TESTS TO BE RUN IN THE LAB

Enter the group code from the DCLS catalog of services which contains the analysis desired. If you have questions concerning the appropriate group code, contact DCLS using the contact list.

#### OBSERVATIONS & FIELD TESTS (optional)

Enter field observations or field tests. These should be entered in the field log and on the lab sheets as well.

RELINQUISHED BY, DATE/TIME, RECEIVED BY:

This area is used to record transfers of the sample custody. The person with custody of the samples (initially the collector) must relinquish the sample custody in the presence of the person receiving custody of the samples (except when shipping samples to lab). This is accomplished by the custodian signing the COCR form in “relinquished by” section and entering the date and time. The new custodian must sign the COCR form in the “received by” section in the company of the original custodian. This process is followed in any subsequent changes in sample custody. Space is provided for four such transactions plus the final acceptance of custody by lab and the date and time the samples are received by lab.

SHIPPING SEAL RECEIVED INTACT, NO. OF, LAB REMARKS

This area is used by lab to record the number of the seal broken to gain access to the contents of the cooler. They will note if the seal is intact. They will also note any other remarks such as the condition of the samples, ice present, etc.

Using CEDS

CEDS can be used for shipping sample information to lab and for printing the COCR from the field data entered in the field data screen.

Since the COCR is printed from CEDS after returning from the field, this method may not be used when sample custody is transferred from person to person in the field.

When using CEDS for shipping sample information to the lab, stations must be established in the station screen and all the pertinent information must be entered in the field data screen using established protocols. Additionally, you will need to **record the Shipping Seal Number** you will be using on the cooler and the **Shipped Date**. Review the information on-screen with the information on the sample tags and in the field log before printing the COCR form. Information on the COCR form may be changed in CEDS and reprinted if errors are made up until the time that the data is shipped to lab. Click on the <PRINT CHAIN CUST> button on the field data screen to print the COCR form. Three copies will be printed.

**Sign one copy** as “Relinquished by:” and complete the date/time at which the samples are relinquished or locked in the cooler. Place it inside the cooler in a Ziploc type waterproof container.

One copy is put in a Ziploc type waterproof cover and is taped to the outside front of the cooler.

The collector retains one copy with the field log.

Multiple-part Preprinted Form

Complete the multi-part form using the definitions above. All sections not indicated as optional must be completed. Make certain that the information on the form exactly matches the information on the sample tags, the field log, and the labsheets. Minor

mistakes made while filling out the form may be corrected by crossing them out and initialing the crossed-out portion. Major mistakes will require a new form to be completed. The form with the mistake must be destroyed.

Sign the bottom portion of the COCR as “Relinquished by:” and complete the date/time at which the samples are relinquished or locked in the cooler.

The original signed copy is to be sent inside the cooler in a Ziploc type waterproof container. The collector retains one copy.

### Preparing Samples for Shipment

Before shipping samples make absolutely sure that the information on the sample tags exactly matches the information on the COCR, the field log, and either lab sheets or the CEDS field data entry screen.

Individual samples must be sealed with a custody seal tape or evidence tape in such a way as to prevent the caps from working loose and the sample tags from coming off. This is generally accomplished by wrapping the wire sample tag securely around the neck of the sample container and leaving the ends of the wires exposed. The tape is then used to tightly span between moving and stationary parts of the sample cap securing the ends of the wire under the tape.

Put samples in a large waterproof bag and put into shipping cooler. Ice samples by putting the ice between the cooler and the waterproof bag. The maximum weight of the cooler is 60#.

Record the wire shipping container seal number on the COCR. Put the original signed copy of the COCR form inside the cooler inside of a waterproof Ziploc type bag. If used, include the lab sheets inside the Ziploc bag as well. Close and lock the cooler by closing the hasp (the bail over the eyelet) and securing it using the padlock supplied by lab. Put the wire seal individually through both the bail and the eyelet of the hasp. Do not put the wire seal through the eyelet in the same manner as the lock. Before closing the wire seal, make absolutely sure the serial number of the wire seal matches the number entered on the COCR form.

The sealed, locked cooler containing the signed COCR form may be placed in the regionally designated location to be picked up by the courier. The sealed, locked cooler is considered to now be under the custody of lab.

### Problems

The sample tags don't match either the CEDS information or the lab sheets, or the COCR form.

The collector can correct these errors only if their field log contains information that will rectify the error. A correction of this type must be meticulously documented in the field log. Only the collector can make changes of this type. If the samples have been shipped, the collector will have to go to lab to make the corrections.

Cooler is locked before all the samples are placed inside.

The collector must develop a separate COCR for the additional samples and ship them in a separate COC cooler. The samples listed on the first cooler's COCR but missing will be marked as not received by lab. The change in coolers' contents must be documented in the field log.

Cooler is sealed but not locked before all the samples are placed inside.

The seal may be broken to inspect the cooler contents and to add or remove samples prior to padlocking the shipment. If the seal is broken, a new COCR must be developed. In CEDS, return to the field data screen (prior to data shipment @ 0900 and 2200, check for the lab send date in the CEDS field data screen), change the seal number, print a new COCR and replace all three of the original COCRs.

When using lab sheets, you may change the seal number on each of the three copies of the form and initial the change on each sheet. This change should be documented in the field log as well.

You don't have any wire seals.

You or someone else who assumes custody of the samples must accompany the samples to DCLS. Samples delivered by the sample custodian don't require locks or custody seals. They do require container seals.

The wrong wire seal number is recorded on the COCR.

If the cooler is locked, you must accompany the samples to DCLS.

If the cooler is not locked you may change the wire seal. (*see above, breaking the wire seal*)

### The Personal Field Log

The personal field log is a legal document used to record information concerning all aspects of an investigation. The log must have bound and numbered pages. The log should be kept in a secure place. Only the owner of book should make notations in the personal field log.

At a minimum, the field log should be used to record information which links that section of the field log with the information found on the COCR. The following information should be used as page headers:

Investigation identification information such as PC, or permit number

Date of investigation

The field log should also contain information that supports but does not duplicate information found on the COCR. This includes, but is not limited to:

Names, addresses, phone numbers of complainant, permit holder, operators, etc.  
Detailed descriptions of the sampling sites  
Variations if any from the WQA SOP manual  
Types of samples collected (grab, straight timed composite including time frame, volume weighted composite, cross-section composite, vertically integrated composite  
Pre and post meter calibration information  
QAQC samples collected  
Detailed observations of the site including physical lay of the land such as upstream, up-gradient, east/west, etc.  
Detailed information included as comments in CEDS or on the lab sheets such as “expect high BOD”  
Documentation of changes to the COCR.

## **4 Field Quality Control Samples**

### ***4.1 Quality control samples for water matrix***

#### **4.1.1 General**

**There are specific requirements for entering QA/QC samples into the WQM module of CEDS. See Appendix D for details.**

Analyte-free water (e.g. deionized or distilled water) is water in which all analytes of interest and all interferences are below method detection limits.

Analyte-free water shall always be used for blank preparation and for the final in-house decontamination rinse.

Analyte-free water shall be transported to the field in containers of suitable construction, such as cubitainers or large plastic jars.

Generally, equipment blanks and field split samples are collected at the same station.

##### **4.1.1.1 Equipment blanks**

Equipment blanks can check for carryover contamination between sampling sites or for the effectiveness of cleaning procedures. For WQM programs using the bucket to obtain samples, the equipment blank needs to check for carryover contamination. Equipment blanks are samples generated from the sampling equipment in use.

Equipment blanks need to be collected in the field between stations.

An equipment blank needs to be collected once for each 25 sites sampled (4%).

Flush or rinse sampler with analyte free water at least once (just as rinse the bucket with sample water) prior to collecting the equipment blank. For the pump and hose method, first by rinsing the outside of the pump and hose intake assembly with analyte free water then rinse the pump and hose as before using at least 5 gallons of analyte free water.

Analyte- free water is run through the sampling equipment (pump and hose, bucket etc.) and then pour or transfer into the respective sampling containers, preserved identically as samples normally collected and then sent to the lab to determine possible contaminants from sampling equipment.

If the equipment blank result is three times higher than the method detection limit, the data collected on that particular date are considered suspect and will be removed from the database by the QA Coordinator.

#### **4.1.1.2 Field split samples**

Split samples are two or more samples collected to determine sampling technique precision and/or laboratory precision. Sampling technique precision is determined by the collection of split samples.

A field split sample needs to be collected once for each 25 sites sampled (4%).

The stations in which split samples will be collected will be chosen randomly.

Using the appropriate sampling technique, obtain one bucket of water and fill two identical containers sequentially.

If the pump and hose is used, containers can be filled using one of the two methods: one method is to place the identical S1 and S2 sample containers side by side and rapidly move the hose discharge back and forth across the tops of the containers until both containers are filled. Repeat the process for each required sample container. Another method uses a Y-fitting so the samples can be collected simultaneously. When using the Y-fitting keep the discharge as level as possible so that discharge stream is divided as equally into each of the containers and the containers fill at the same rate.

Collect bacteriological split samples side by side directly from the source.

Split samples will be collected, preserved and handled in accordance with the procedures in this manual.

### ***4.2 Quality control samples for sediments***

#### **4.2.1 Equipment blanks**

Equipment blanks can check for carryover contamination between sampling sites or for the effectiveness of cleaning procedures. Equipment blanks are samples generated through the sampling equipment in use. To avoid having to clean equipment between the stations, getting enough equipment (i.e. grabs, dredges) for the entire sampling event is strongly recommended. If staff can bring enough equipment for an entire sampling event, the possibility of carryover contamination is removed and the equipment blank for sediment collection then becomes a check on the cleaning procedures. In that instance, the equipment blank may be performed in the field at first station prior to sampling or in the laboratory. Equipment blanks need to be collected once per batch of cleaning.

If there is not enough equipment to sample multiple stations, the equipment must be cleaned in the field between each station and two equipment blanks must be collected: one prior to sampling (to check the effectiveness of the cleaning procedures) and the other between two stations in the field (to check for carryover contamination).

To collect an equipment blank, run analyte-free water through all the sampling equipment that comes in contact with the sample and collect all the rinsate in a pre-cleaned stainless steel or Teflon tray. Transfer the rinsate from the tray to a sediment container and submit it for analysis.

If the equipment blank results are three times higher than the method detection limits, the data collected on that particular date are suspect and will be removed from the database by the QA Coordinator.

#### **4.2.2 Field split sediment samples**

Ten percent of the sediment samples collected will be field split samples.

The split samples will be collected from a single site as one large sample with sufficient volume to be halved into two separate samples of equal volume. Homogenize the sample prior and splitting it into two jars for analysis.

Split samples will be collected and handled in accordance with the collection of regular samples as described earlier in this manual.

The station in which split samples will be collected will be chosen randomly.

## **5 Field Testing Procedures**

### **5.1 Accument AP series handheld pH/mV/Ion meter**

#### **5.1.1 Scope and Application**

This method is an electrometric procedure for measuring pH in surface and saline water samples.

#### **5.1.2 Procedure**

##### **5.1.2.1 General procedures and precautions**

- Rinse the electrodes thoroughly with distilled water after each sample or standard. Shake off excess water and blot dry.
- Calibrate the meter each day before use with a minimum of two fresh standard buffer solutions that bracket the expected pH of the samples to be tested
- If the sample pH reading is beyond the calibration standard value, recalibrate the meter with standards to bracket the sample pH. Previous measurements may need to be excluded.
- After reading highly acidic or alkaline samples, rinse electrodes thoroughly with distilled water and check electrode response and calibration linearity. Allow additional time for equilibration.
- Be sure to check the expiration dates on the pH buffers prior to using them for calibration/post-calibration.
- The pH probe generally has a one-year shelf life.

##### **5.1.2.2 Instrument setup**

1. For pH, mV, and Ion measurements, attach combination electrodes with BNC connectors directly to the middle BNC jack on the meter. If non-combination electrodes are used, adapters must be used.
2. If automatic temperature compensation is desired, insert the waterproof ATC connector into the ATC tower jack. Insert the attached plug if an ATC probe is not used to maintain a waterproof state.

3. The AC adapter jack lies next to the BNC jack opposite the tall ATC tower jack. Insert the attached plug to maintain the meter in a waterproof state. If an AC adapter is connected, the meter is not waterproof. When the AC adapter is in use, the battery is removed from the circuit, preventing battery drainage.
4. Press the on/off button to turn on the meter. Press setup twice and then enter to clear memory.
5. With the electrodes immersed in storage or buffer solution, press pH to enter the pH mode.

### **5.1.2.3 Instrument calibration**

1. For the first use of the day, press the setup key twice and then hit enter to clear the previous calibration data.
2. Press the mode key until the display indicates the instrument is in pH mode. Remove protective cap from electrode, rinse with distilled water and blot excess water with soft tissue.
3. Immerse electrode in the first buffer solution and stir briefly with electrode to remove bubbles from the electrode surface. If possible a magnetic stirrer should be used with all samples to insure homogenous mixing of solutions.
4. Depress the standard key and continue stirring. Be sure that the ATC probe is also immersed in the buffer solution. The standard 1 symbol and value should flash. When a stable reading is achieved, the auto symbol will stop flashing and the standard buffer value is displayed.
5. Press std to access the Standardize screen. The buffer group used by the meter will briefly be displayed, and the prompt press std to standardize will flash.
6. Press std again to initiate standardization. The meter will automatically recognize the buffer used, and display the value on the screen. Standardize will flash until the buffer is accepted, and the meter returns to the Measure screen. The accepted buffer value remains displayed on the screen.
7. Repeat steps 2-4 with a second and subsequent buffers. When the meter accepts the second buffer, it will briefly display the efficiency (as percent slope) associated with the electrode's performance prior to returning to the Measure mode. If the percent slope is outside the range of 90-102, the meter will

display ELECTRODE ERROR and will not return to the Measure screen until you press enter. The message ELECTRODE ERROR will remain until an acceptable slope is attained after standardization.

8. Record all pH values onto the logsheet.
9. Place the plastic protective cap over the probe for transport. Make sure the cotton is saturated and placed in the bottom of the cap.

#### **5.1.2.4 Field measurement procedures**

1. If the instrument has been checked and calibrated, depress the on/off key to switch unit on.
2. Immerse the electrode into the sample solution. Stir moderately if possible. Note: Make sure the meter is in the pH mode.
3. When the meter senses that the reading is stable, STABLE will appear under the measurement reading. The reading may be recorded at this time.
4. If AUTO is not displayed on the screen, the autoread function is not active, and the meter will continuously monitor the pH value of the sample, and change as it changes.
5. If AUTO is displayed on the screen, the meter will fix the measured pH value on the screen when it is stable. AUTO will flash on the display until a stable reading is obtained.
6. Place the plastic protective cap on the probe making sure that the tissue is saturated

#### **5.1.2.5 QC limits**

Check calibrations using standard buffer solutions at least once during or at the end of the sampling, and record the results in the calibration logsheet (see Appendix A). If the reading is off by more than  $\pm 0.2$  pH units, corrective action needs to be taken. The data collected during the day needs to be flagged.

#### **5.1.2.6 Preventative maintenance**

##### ***5.1.2.6.1 Battery requirements***

- ◆ The pH meter is powered by a 9-volt battery.

#### ***5.1.2.6.2 Replacing batteries***

- ◆ The battery must be installed or replaced (1) prior to initial use, (2) when the main display area is blank, or (3) when the Low Battery (Lo?) indicator is on.

To install or replace the battery:

1. Remove the battery slipcover from the back of the meter.
2. Disconnect the old battery, and connect a new 9-volt battery.
3. Place the installed battery in meter battery compartment. Make certain that the battery wires are properly positioned so as not to interfere with the closing of the battery cover. Otherwise, the cover's edge may damage the wires.
4. Replace the battery slipcover.
5. If you desire to use line voltage, connect the AC adapter to the top connector AC power jack and to a power source. Note that the meter is not waterproof when the AC adapter is connected.

#### ***5.1.2.6.3 Instrument electronics check***

Check the instrument for proper operation at least once a month using the following procedures. The results should be recorded in the logsheet.

1. Disconnect the electrode cable from the meter. Press I, turn on the meter, then press C to clear. The display should show C and Auto symbol. If not, replace the batteries.
2. Insert one end of a paper clip into the small hole in the center of the 'pH' input connector.
3. Press 'pH' then 'STD'. The display should lock at pH 7.00, indicating a one-point standardization. If the meter fails, call the manufacturer for service.
4. Reconnect the pH electrode cable to the "pH" input connector. Insert one end of a paper clip into the small hole in the center of the electrode connector. Hold the

other end of the clip to the inside barrel of the same connector.

5. Press 'pH' then 'STD'. The display should lock at pH 7.00. Press 'pH' then remove the paper clip. The reading should drift. If the meter fails, call the manufacturer for service.
6. Reconnect the pH electrode. Immerse the electrode in the pH 4 buffer and perform a one-point standardization. Then immerse the electrode in the pH 10 buffer and take a pH reading. At 25°C, the reading should be between 9.7 and 10.1 pH. If the test fails, the pH electrode is faulty and must be rejuvenated or replaced

#### ***5.1.2.6.4 pH electrode rejuvenation***

1. This meter can be directly fitted with combination electrodes only. If separate pH or ION and reference electrodes are employed, adapters are required. The meter also provides a jack for an ATC probe.
2. Carefully remove the protective cover from the end of the pH electrode. Before using the electrode, or if the electrode is dry, soak it for 2-4 hours in electrode storage solution, pH 4 buffer, or KCl solution.
3. Prepare and condition the ion selective electrode as recommended by the manufacturer.
4. Remove the shorting cap from the BNC connector. Install the electrode by twisting it to lock it in place.
5. Rinse and blot dry (don't wipe) the electrode between each measurement. Use distilled or analyte free water, or a portion of the next solution to be measured.
6. Between measurements, store the pH electrode in electrode storage solution, pH 4 buffer, or KCl solution. If liquid filled, always leave the filling hole open whenever the electrode is immersed in any solution. Refill when the level of fill solution recedes below the manufacturers recommended level.
7. Store your ion selective electrode as recommended by the manufacturer.

#### **5.1.2.6.5 Spare parts and supplies**

1. Buffer solutions pH 4, 7 & 10
2. Kim wipes or soft cloth
3. 9- Volt batteries
4. Automatic Temperature Adapter (ATC)
5. Combination liquid-filled pH/ATC electrode
6. AC adapter
7. Adapter (US Standard/Pin to BNC)
8. Adapter (dual pins to BNC)
9. Adapter (BNC/pin to single BNC)

#### **5.1.2.6.6 Reference**

Accumet AP Series Handheld pH/mV/Ion Meter  
Instruction Manual, Fisher Scientific, 1998.

### **5.2 YSI Model 58 Dissolved Oxygen and Temperature Meter**

#### **5.2.1 Instrument check**

Before using the instrument, check the membrane selection switch to ensure it corresponds to the membrane used on the probe.

Check the probe for:

Condition of the membrane (wrinkled, dried out, air bubble)  
Condition of the gold cathode (tarnished or silver plating)  
Condition of the silver anode (discoloration)

Check the probe connection for security and tightness

Turn the instrument function switch to the zero position and allow the meter to stabilize for at least 15 minutes.

Daily Calibration

Calibrate the meter daily when in use. Calibration can be disturbed by physical shock, touching the membrane, fouling of the membrane or the drying out of the electrolyte solution.

Air calibration is normally easiest since the instrument compensates for temperature variation in that mode. However, the operator may elect to calibrate in the mg/l mode if he intends to take measurements in that mode, since doing so will eliminate any possible mode to mode error.

Air calibration (% Saturation)

Air calibration is the quickest and by far the simplest calibration technique

Turn the instrument function switch to the % saturation setting.

Place a moist sponge or a piece of cloth in the plastic calibration bottle. Loosen the bottle lid about ½ turn and slip the bottle over the probe guard up to the bottle. Place the probe in a protected location at room temperature.

Set the function switch to ZERO and readjust the display to read 0.00. Switch back to % air saturation mode.

After the display reading stabilizes unlock the O2 calibration control knob locking ring.

Adjust the display to the calibration value indicated in the pressure/altitude chart printed on the back of the meter.

Re-lock the locking ring of the O2 calibration control knob to prevent accidental changes in the calibration setting.

Record the % saturated DO into the logsheet.

Air saturated water calibration

Alternatively calibrate the meter probe to mg/l measurements using the following procedures:

Air saturate a volume of water by aerating for at least 15 minutes at a constant temperature.

Place the probe in the sample and stir. Switch the function switch to TEMP.

From the oxygen solubility chart printed on the back of the meter determine and record the mg/l value corresponding to the temperature indicated.

Determine the local altitude or the true atmospheric pressure. Using the pressure/altitude chart on the back of the meter, determine the correct calibration value.

Multiply the mg/l value from the oxygen solubility table by the calibration value from the pressure/altitude table and divide by 100 to determine the correct mg/l oxygen content of the saturated sample.

Readjust to zero if necessary.

Check that the salinity knob is set at 0.

Turn the function switch to 0.1 or 0.001 mg/l setting.

Unlock the O2 calibration control knob locking ring.

Adjust the display to the value calculated previously.

Allow two minutes to verify stability of the readings.

Readjust as necessary.

Relock the locking ring of the O<sub>2</sub> calibration control knob to prevent accidental changes to the calibration settings.

Field measurement procedures

D.O. Measurement Procedures

With the instrument prepared for use and the probe calibrated, place the probe in the sample. If the stirrer is to be used, connect it and turn the stirrer switch to ON.

Adjust the salinity control to the salinity of the sample.

Turn the meter function switch to ZERO and zero the meter with the O<sub>2</sub> ZERO knob if necessary.

Turn the meter function switch to the desired readout setting and read the D.O. value in mg/l when the meter reading has stabilized.

Maintenance

Field probe maintenance

Membrane life depends on usage. The average useful life is 2-4 weeks. However, membrane replacement may be required whenever large bubbles form in the electrolyte solution or if the membrane becomes fouled or damaged. Membrane replacement may be required if erratic readings are observed or the calibration is not stable.

Electrolyte solution can be prepared by making a saturated solution of reagent grade KCL and distilled water, and then diluting the solution 1:1 with distilled water. Adding two drops of Kodak photoflow per 100 ml of solution assures good wetting of the sensor but is not absolutely essential.

The gold cathode should always be bright and untarnished. Inspect the gold cathode whenever the membrane is changed. If tarnished, clean by wiping with a clean lint-free cloth, pencil eraser or hard paper. Rinse the sensor several times with the electrolyte solution, refill and install a new membrane.

Some gases can contaminate the sensor. This is evidenced by discoloration of the gold cathode. If the tarnish can not be removed by conventional methods, return the probe to the factory for service

Probe performance checks

Every month when the probe is in daily use or whenever the probe response is slow or calibration is unstable, check the probe performance.

Speed of response

Prepare and calibrate the probe.

With the probe in air, switch to the % air saturation mode.

Immerse the probe in a 25°C O<sub>2</sub>-depleted sample (2 g/l Sodium Sulfide).

A proper functioning probe will down scale to 10% air saturation in 20 seconds or less.

Background current

After performing the speed of response steps, leave the probe in the depleted sample for approximately five minutes. The reading should fall below 1-% air saturation.

Calibration stability

Carefully calibrate the probe in moist air inside the calibration bottle with the instrument set in the % air saturation mode.

Allow the instrument to operate for one hour and recheck the calibration.

A properly functioning probe will hold calibration within  $\pm 1\%$  for one hour after the first hour of operation

Probe Service

If any of the following conditions arise, the probe should be serviced accordingly:

Damaged or wrinkled membrane. Change the membrane and reset.

Fouled or silver coated gold cathode. Change the cathode.

Fouled silver anode. Soak for 24 hours in 3% ammonia, rinse thorough with distilled water and retest.

Damaged cable or connector. Inspect and replace if needed.

If these steps do not restore the probe's performance to specifications, return the probe to the factory to be serviced.

Meter maintenance

When the Lobat warning shows on the display there are 50 hours of use remaining. This warning reminds the operator to change the batteries at their earliest convenience.

The instrument uses 4D sized carbon-zinc batteries. These batteries are located in the upper holder of the instrument. Remove the batteries if the instrument will be unused for long periods of time

Quality Control

DO meter calibration checks

Daily

Calibrate the meter in accordance with the procedures of this manual.

Check the calibration at least once during sampling and at the conclusion of the day's sampling. Record the data onto the logsheet. If a calibration check is off  $\pm 5\%$  of the calibration value, a corrective action needs to be taken. The data collected during that day needs to be flagged.

Monthly

Fill a clean bucket with uncontaminated or analyte free water and place the probe into the bucket. Rinse the BOD bottle 1 or 2 times with the water from the bucket, discarding the

rinse. Enter BOD bottle horizontally, avoid introducing air bubble into BOD bottle.  
Determine the DO by the Winkler method (see the method procedure in section V)

If the air calibration seems to operate properly but the oxygen concentration disagrees with the average results of the Winkler value by more than 0.5 mg/l, it is time to have the electrode or meter serviced or replaced.

#### Temperature Verification

Central Office personnel will conduct temperature verification for thermistor against an NIST certified thermometer annually

Regions should check the temperature probe against another multiprobe instrument's temperature probe semi-annually. If a discrepancy should occur (temperatures are not +/- 1°C) contact Central Office so that the probes can be checked against an NIST certified thermometer as soon as possible. If there is good agreement between the instruments, then central office personnel

The temperature verification should be conducted against three points such as an ice/water mixture (e.g. 4°C), room water temperature (e.g. 25°C) and at a warm water temperature that will best approximate the highest ambient temperature expected to be sampled (e.g. 30°C). The thermistor and certified thermometer are lowered side by side into a waterbath, allowed to stabilize and then temperatures are read from both.

If the difference between traceable certified thermometer and thermistor values more than 0.5°C, the thermistor should not be used and should be sent back to the manufacturer for the thermistor to be replaced.

### ***5.3 YSI 85 Handheld Oxygen, Conductivity, Salinity and Temperature System***

#### **5.3.1 Preparing the probe**

The YSI Model 85 dissolved oxygen probe is shipped dry. The protective membrane cap on the probe tip must be removed and replaced with KCl solution and a new membrane cap before using the probe. Follow the instructions below to install KCl solution and the new membrane cap

##### **5.3.1.1 Membrane installation**

1. Unscrew and remove the probe sensor guard.
2. Unscrew and remove the old membrane cap.
3. Thoroughly rinse sensor tip with analyte-free water.

4. Prepare the electrolyte solution according to the directions on the KCl solution bottle.
5. Hold the membrane cap and fill it at least  $\frac{1}{2}$  full with the electrolyte solution.
6. Screw the membrane cap onto the probe until it is moderately tight. A small amount of electrolyte solution should overflow.
7. Screw the probe sensor guard on until it is moderately tight

### **5.3.2 Calibration**

#### **5.3.2.1 Calibration of Dissolved Oxygen**

1. Ensure that the sponge inside the instrument's calibration chamber is wet. Insert the probe into the calibration chamber.
2. Turn the instrument on by pressing the ON/OFF button on the front of the instrument. Press the MODE button until dissolved oxygen is displayed in mg/l or %. Wait for the dissolved oxygen and temperature readings to stabilize (usually 15 minutes is required).
3. Use two fingers to press and release both the UP ARROW and DOWN ARROW buttons at the same time.
4. The LCD will prompt you to enter the local altitude in hundreds of feet. Use the arrow keys to increase or decrease the altitude. When the proper altitude appears on the LCD, press the ENTER button once.
5. The instrument should now display CAL in the lower left of the display. The calibration value should be displayed in the lower right of the display and the current % reading should be on the main display. Make sure that current % reading is stable, then press the ENTER button. The display should read SAVE then should return to the normal operation mode.
6. Record the % saturated DO onto the logsheet.

#### **5.3.2.2 Calibration of Conductivity**

1. Turn the instrument on and allow it to complete its self-test procedure.
2. Select a calibration solution, which is most similar to the sample you will measure.

3. Place at least 3 inches of solution in a clean glass beaker.
4. Use the Mode button to advance the instrument to display conductivity.
5. Insert the probe into a beaker deep enough to completely cover the oval shaped hole on the side of the probe. Do not rest the probe on the bottom of the container. Suspend it above the bottom by at least ¼ inch.
6. Allow at least 60 seconds for the temperature reading to become stable.
7. Move the probe vigorously from side to side to dislodge any air bubbles from the electrodes.
8. Press and release the UP ARROW and DOWN ARROW buttons at the same time.
9. Use the UP ARROW and DOWN ARROW button to adjust the reading on the display until it matches the value of the calibration solution you are using.
10. Once the display reads the exact value of the calibration solution being used, press the ENTER button once. The word "SAVE" will flash across the display for a second indicating that calibration has been accepted.
11. Record the calibration value into the logsheet.

### 5.3.3 Taking Measurements

Once the batteries are installed correctly, press the ON/OFF button. The instrument will activate all segments of the display for a few seconds, which will be followed by a self-test procedure that will last for several more seconds. During the power on self-test sequence, the instrument's microprocessor is verifying that the instrument is working properly. The instrument will display the cell constant of the conductivity probe when the self-test is completed. If the instrument detects an internal problem, the display shows a continuous error message.

The Model 85 is designed to provide six measurements: Dissolved Oxygen %, Dissolved Oxygen mg/l, Conductivity, Specific Conductance, Temperature and Salinity. To choose one of the measurement modes above (temperature is always displayed) simply press and release the MODE button.

It is important to remember that the dissolved oxygen probe's accuracy is stirring dependent. This is due to the consumption of oxygen at the sensor tip during measurement. When taking dissolved oxygen measurements the probe must be moved through the sample at the rate of 1 foot per second to provide adequate stirring.

### **5.3.4 Quality Control**

#### **5.3.4.1 DO and conductivity meter calibration checks**

##### ***5.3.4.1.1 Daily***

- ◆ Calibrate the meter in accordance with the procedures of this manual.
- ◆ Check the calibration at least once during sampling and at the conclusion of the day's sampling. Record the data onto the logsheet. If calibration check is off  $\pm 5\%$  of the calibration value, corrective action needs to be taken. The data collected during that day needs to be flagged.

##### ***5.3.4.1.2 Monthly***

1. Fill a clean bucket with uncontaminated or analyte free water and place the probe into the bucket. Rinse the BOD bottle 1 or 2 times with the water from the bucket, discarding the rinse. Submerge the BOD bottle horizontally to avoid introducing air bubbles into the BOD bottle. Determine the DO by the Winkler method (see method procedure in Section V)
2. If the air calibration seems to operate properly but the oxygen concentration disagrees with the average results of the Winkler value by more than 0.5 mg/l, it is time to have the electrode or meter serviced or replaced.

#### **5.3.4.2 Thermistor Verification**

Central Office personnel will conduct temperature verification for thermistor against an NIST certified thermometer annually

Regions should check the temperature probe against another multiprobe instrument's temperature probe semi-annually. If a discrepancy should occur (temperatures are not  $\pm 1^{\circ}\text{C}$ ) contact Central Office so that the probes can be checked against an NIST certified

thermometer as soon as possible. If there is good agreement between the instruments, then central office personnel

The temperature verification should be conducted against three points such as an ice/water mixture (e.g. 4°C), room water temperature (e.g. 25°C) and at a warm water temperature that will best approximate the highest ambient temperature expected to be sampled (e.g. 30°C). The thermistor and certified thermometer are laid side by side into a waterbath, allowed to stabilize and then temperatures are read from both.

If the difference between traceable certified thermometer and thermistor values more than 0.5°C, the thermistor should not be used and should be sent back to the manufacturer for the thermistor to be replaced.

## ***5.4 Hydrolab H2O Water Quality Multiprobe with Display***

### **5.4.1 System components**

The four basic components of the Hydrolab water quality multiprobe are the probe, the display unit, the sample circulator and the battery pack.

- a. The multiprobe, in its sealed high pressure housing, contains all of the sensors for temperature, dissolved oxygen, conductivity, pH, and depth as well as the electronic circuits that sensors require for their operation. The sensors, in combination with the electronic circuits, provide the data signals that represent the values of the measured parameters.
- b. The display unit which operates at the opposite end of the data cable from the multiprobe. Depending upon the setting of its function key, the display unit sends signals down the cable directing the multiprobe to make a measurement of the selected parameter.
- c. The sample circulator is an electrically powered magnetic stirrer similar to laboratory magnetic stirrers. It is encased in a high-pressure weighted housing, which permits underwater operation.
- d. The auxiliary battery pack supplies power from a 12 volts recharger for the entire system.

## 5.4.2 Calibration of Parameters

### 5.4.2.1 General Procedures

- Note: DO NOT turn off the display unit at any time during the calibration procedure. The newly calibrated data will not be saved if the unit is turned off.
- Note: Maintain a calibration log sheet in which is entered all data pertaining to each precalibration, postcheck, or maintenance procedure.
- Calibration and postcheck procedures should be performed on each day of use. The calibration parameter sequencing provided below follows the manufacturer's recommendations. However, only the calibration sequence for specific conductance and pH are crucial to proper instrument operation.
- Replace storage cup on multiprobe with bottomless calibration cup. Take special care not to bump probes with hand or cup as this may result to damage to the probes.
- After the calibration of each parameter, record the calibrated parameter value in the calibration sheet (in Appendix A) and be sure to store the data utilizing the display unit.
- When the multiprobe battery reading drops below 10.0 volts, the scout 2 internal batteries should be replaced or external battery recharged as soon as possible after the low battery warning symbol appears for optimum system performance.
- Check the expiration dates on all pH standards.
- Specific Conductance standards should be fresh to within 6 months of the date of preparation

### 5.4.2.2 Dissolved Oxygen

- Note: It is good practice to get analyte-free water for calibration from carboy. The analyte-free water is stabilized to room temperature so the temperature equilibrium time will be reduced.
1. Check the membrane on the probe tip to see if it is wrinkled, bubbled, torn, dirty, or otherwise damaged. If so, service the probe in accordance with the manufacturer's operation manual. It is, however, good practice to replace the membrane on a regular schedule, before trouble becomes visible. Frequent

changes of the electrolyte solution will maximize the life of the sensor.

2. With the multiprobe oriented so that the sensors are pointed toward the ceiling, fill the calibration cup with analyte-free water until the water is just level with the O-ring used to secure the membrane.
  3. Carefully remove any water droplets from the membrane with the corner of a tissue (DO NOT apply pressure to surface) and cover the open top of the calibration cup to prevent air currents from affecting calibration.
  4. Determine the laboratory barometric pressure in mm Hg from a barometer and record the data in the appropriate spaces on the data sheet.
  5. Turn on the Scout 2 unit with the on/off button. Wait for 5 minutes to allow air in the cup to become water saturated. The sensor is ready for calibration once the readings have stabilized. Record the initial meter dissolved oxygen reading on the meter calibration log sheet.
  6. Determine the temperature from the Sonde and record the data in the appropriate space on the data sheet. Read the Oxygen concentration from the table based on temp in Celsius degrees as determined by the far left column and first row of the chart. Multiply the Oxygen concentration by the correction factor as determined by the barometric pressure (mmHg). Press calibrate and use right arrow key to choose (%). Press in the barometric pressure in mmHg from a barometer or the calculated value. Press enter; Use left arrow key to choose (yes) to save the calibration. The unit will send a DO value (mg/l) to display. Press screen and note that %Sat equals 100.0 for correct DO calibration. Read the value of DO mg/l from screen and record in the appropriate space on the logsheet. Compare the value of table DO and Sonde DO. They must compare within  $\pm 0.5\text{mg/l}$ .
- Note: The conversion factor from inHg to mmHg is 25.4.

#### 5.4.2.3 Specific Conductance

- Note: Readings are most accurate when they lie within the calibrated range. Determine the expected range of values in the field prior to calibration.

1. Rinse the sensors twice with a small portion of the specific conductance standard to be used for calibration, discarding the rinse each time.
  2. With the calibration cup screwed onto the multiprobe, sensors pointed toward the ceiling. Fill calibration cup with fresh standard solution to about one centimeter below the top. Be sure no bubbles are trapped in the bores of the cellblock.
  3. Watch the specific conductance readings until they have stabilized; the sensor is now ready for calibration. Record the initial meter specific conductance reading on the meter calibration log sheet.
  4. Press calibration and use the left arrow key to choose c press enter. Use up, down, and right arrows to enter the value of your specific conductance standard. Press enter. Use the left arrow key to choose Y (yes) to save the calibration. The unit will send the standard value to display. Record the standard value in the logsheet.
  5. Pour standard solution into a storage bottle for use as the standard rinse in the next calibration. Discard after using for the rinse.
- Note: The following table shows several potassium chloride solutions and their specific conductance values.

KCL Molar Concentration	Specific Conductance in (ms/cm)
0.5M	58.64
0.1M	12.90
0.05M	6.668
0.01M	1.413
0.005M	0.718
0.001M	0.147

#### 5.4.2.4 pH

- Note: Calibrate the instrument with pH buffer that brackets the range of values anticipated in the field.
1. Flush the calibration cup and sensors thoroughly 3 times with analyte-free water.
  2. Rinse twice with a small amount of pH 7.0 buffer saved from previous calibrations to saturate the sensors. Discard the buffer after each rinse.
  3. Fill cup with Fresh pH 7.0 buffer sufficient to cover the sensor.
  4. Allow two minutes for thermal equilibrium. Record the pH value displayed in the logsheet.
  5. Press calibrate and enter choose (P). Use the up, down, and right arrows to enter the pH of the zero standard (7.00), presses enter. Use the left arrow to choose Y (yes) to save calibration. The unit will send a pH value to the display. Record the pH value in the logsheet.
  6. Pour buffer into a storage bottle for use as the rinse in step 2 of the calibration.
  7. Flush the calibration cup and sensors thoroughly twice with analyte-free water.
  8. Rinse the cup and sensors twice with a small amount of pH 10.00 or pH 4.00 buffer.
  9. Fill the calibration cup with FRESH pH 10.00 or pH 4.00 buffer to cover the sensor and wait for the instrument to equilibrate.
  10. Record the pH value displayed in the logsheet.
  11. Press calibrate and enter to choose (P). Use up, down and right arrows to enter the pH of the slope standard, presses enter. Use the left arrow to choose Y (yes) to save calibration. The unit will send a pH value to the display. Record the value in the logsheet.
  12. Pour the buffer into a storage bottle. Flush the calibration cup and sensors thoroughly three times with analyte-free water.

13. Replace the storage cup.
14. Place a sufficient amount of tap water in the storage cup to keep the DO membrane moist. Do not allow the water to come in contact with the sensors as an ionic gradient may develop resulting in dilution of the electrolyte solutions.

#### **5.4.2.5 Thermistor Verification**

Central Office personnel will conduct temperature verification for thermistor against an NIST certified thermometer annually

Regions should check the temperature probe against another multiprobe instrument's temperature probe semi-annually. If a discrepancy should occur (temperatures are not  $\pm 1^{\circ}\text{C}$ ) contact Central Office so that the probes can be checked against an NIST certified thermometer as soon as possible. If there is good agreement between the instruments, then central office personnel will check the instruments against an NIST certified thermometer as planned.

The temperature verification should be conducted against three points such as an ice/water mixture (e.g.  $4^{\circ}\text{C}$ ), room water temperature (e.g.  $25^{\circ}\text{C}$ ) and at a warm water temperature that will best approximate the highest ambient temperature expected to be sampled (e.g.  $30^{\circ}\text{C}$ ). The thermistor and certified thermometer are lowered side by side into a waterbath, allowed to stabilize and then temperatures are read from both.

If the difference between traceable certified thermometer and Hydrolab values more than  $0.5^{\circ}\text{C}$ , the Sonde should not be used and should be sent back to the manufacturer for the thermistor to be replaced.

#### **5.4.2.6 Depth**

Depth should be calibrated to zero in the air, at or near the surface of the water to be sampled.

#### **5.4.3 Unit components**

The basic Hydrolab consists of: the display unit, the data cable, the Sonde, the sample circulator, and the battery pack. If additional weight is needed, a lead weight can be attached to the nylon line.

#### **5.4.4 Preparation for use**

1. Interconnect the display unit, battery pack, and data cable. Carefully place the instrument back in its case. Coil the cable and keep it kink-free.
2. Remove the storage cup from the Sonde and screw on the circulator in its place. Connect the two ends of the data cable to the probe and circulator. Ensure that the probe is attached to the data cable with the pin and clip ring.
3. Fill the Sonde storage bucket with sample water so that the sensors will be submerged. Store the Sonde in a bucket of water when not in use. Alternately, remove circulator (do not disconnect) and replace storage cup filled half full with sample water.
4. Ensure that the magnetically coupled impeller on the stirrer base is properly lubricated and rotating free on its shaft. Any obstruction to smooth rotation of the impeller may cause erratic DO measurements and excessive power drains to the battery.
5. Turn the display unit switch to OFF.

#### **5.4.5 Field set-up and operation**

While the unit is in operation aboard the vessel, the boat operator must maintain the boat's position and orientation with wind and tide movement to ensure that the Sonde hangs as vertically as possible.

While the unit is in the operation aboard the vessel, keep the probe away from the engine's propeller to ensure the safety of the Sonde and data cable, and to prevent interference from the propeller wash with all water quality measurements.

Remove the unit from storage.

Screw on the circulator. – Remove the storage cup from the Sonde and screw on the circulator in its place. Caution should be taken to avoid any contact with the sensors.

Connect the two ends of the data cable to the probe and circulator. – Ensure that the probe is attached to the data cable with the pin and clip ring.

Calibrate depth. – At the station above the surface water, press the depth key.

When not in use, store the Sonde in the plastic bottle used for DO Saturation checks with a small amount of water or bucket of water.

Visually inspect the magnetic impeller on the stirrer base. – Make sure magnetic impeller is rotating freely on its shaft. Any obstruction to smooth rotation of the impeller may cause erratic DO measurements and excessive power drains to the battery.

Lower the Sonde to 0.3 meter below the surface.

Wait for thermal equilibrium. Allow thermal equilibrium and then verify that the dissolved oxygen reading is stable. The D.O. sensor is the slowest of all the Sonde sensors to equilibrate, therefore, wait for this reading to stabilize before recording it on the field sheet. The field parameter data should be recorded and entered into CEDS to the tenth place (do not round based on the hundredth place).

Turn the display unit off and retrieve the Sonde - At the end of the day put the storage cup back on the Sonde.

#### **5.4.6 DO calibration Confirmation**

A DO % saturation confirmation needs to be performed in the middle of run. The Hydrolab should be stored at 100% air/water saturation environment (e.g. wet towel or bottle with small amount water in it). Allow the probe to equilibrate, record the DO % saturation on the field data sheet then transfer it to CEDS in the comment field. The reading should be  $\pm 5\%$  of the true value. If DO % saturation is out of the specified range, the Hydrolab needs to be recalibrated in the field.

#### **5.4.7 Hydrolab postcheck**

Note: DO NOT CALIBRATE THE INSTRUMENT TO THE STANDARD VALUES DURING POSTCHECK CHECKS. Perform postcheck before cleaning up and servicing the sensor. When performing the postcheck of the system, it is extremely important that the room temperature, Sonde temperature, analyte-free temperature, and all standard solutions are at thermal equilibrium. If thermal equilibrium needs a long time or postcheck values are outside the QC criteria, postcheck on next day is recommended.

##### **5.4.7.1 Dissolved Oxygen**

Follow the procedures described in Section 4.4.2.2.

Record the data on the logsheet. Compare the Saturated DO values from the chart and the instrument values as recorded in the logsheet. If the difference between the two is less than 0.5 mg/L the instrument is in calibration. If the difference between the Saturated DO value and the instrument indicates that the instrument is not in calibration, check again the next morning to make sure that the temperature was properly

equilibrated. If the difference is still greater than 0.5 mg/L the data collected during the sampling event is suspect and will be removed from the database by the QA Coordinator. Additionally, the instrument should not be utilized until more extensive cleaning/maintenance is conducted and the instrument calibrates well.

#### **5.4.7.2 Specific Conductance**

Follow the procedures described in Section 4.4.2.3

Record the data on the logsheet. Compare the displayed value to the standard value and calculate the difference. If the difference is less than  $\pm 10\%$  of 147  $\mu\text{S}/\text{cm}$  standard and  $\pm 5\%$  of 1413  $\mu\text{S}/\text{cm}$ , 12.90  $\text{mS}/\text{cm}$  and 58.6  $\text{mS}/\text{cm}$  standards and the instrument is in calibration. If the instrument is not in calibration, check again the next morning to make sure that the temperature was properly equilibrated. If the difference is still out specification, the data is suspect and will be removed from the database by the QA Coordinator. Additionally, the Hydrolab should not be utilized for that parameter until it has an extensive cleaning/maintenance.

#### **5.4.7.3 pH**

Follow the procedures described in Section 4.4.2.4

Record the data in the logsheet. Compare the displayed values to the standard values. If the difference between the standard utilized and the value displayed is  $\leq 0.2$  units the pH is in calibration. If the difference indicates that the instrument is not in calibration, check again the next morning to make sure that the temperature was properly equilibrated. If the difference is still greater than 0.2 units the data is suspect and will be deleted from the database by the QA Coordinator. Additionally, the Hydrolab should not be utilized for that parameter until it has an extensive cleaning/maintenance.

#### **5.4.8 Preparation of KCL standards**

Note: If the KCL 1 Molar stock solution is purchased from a supplier, be sure to check that the expiration date of the stock solution is still good prior to using it. If a powder is utilized to make the 1 Molar KCL stock solution, be sure not to use the solution after six months of preparation. The dilution water should have a very low conductivity and ultra pure grade water may be obtained for this purpose from DCLS by request.

Prepare the KCL solution to be used in calibration after determining the desired conductivity range. Dilute prepared 1 Molar KCL stock solution to desired molarity using appropriate volumetric glassware.

#### **5.4.8.1 Preparation of 1 Molar KCL stock solution:**

KCL salt is hygroscopic and can change weight in storage. Before making you stock solution, pour a sufficient amount of KCL salt into an aluminum pan or crucible and dry it at 40°C overnight. Place the pan or crucible containing the dried salt in a desiccator and let it sufficiently cool before weighing it.

Turn on analytical balance and open the door. Place the weighing dish on the pan and rezero the analytical balance.

Carefully weigh out exactly 74.557 grams of reagent grade KCL salt on the balance.

Carefully transfer the salt to a 1000 ml class A volumetric flask, rinse the weighing dish with analyte-free water and pour the rinse into the volumetric flask until all the salt has been transferred to the flask. Fill the flask with analyte-free water to the 1000 ml mark and make sure the meniscus lines with the mark.

Invert the volumetric flask several times until KCL salt is completely dissolved.

Label a 1000 ml rectangular storage bottle while waiting for salt to dissolve. Write “1M KCL Stock Solution”, your initial, and date prepared.

Transfer the 1 Molar KCL stock solution to a storage bottle.

#### **5.4.8.2 Preparation of 0.1 Molar KCL standard solution**

Thoroughly mix the 1 Molar KCL stock solution by invert the storage bottle.

Measure out 100 ml of 1 Molar stock solution using a class A 100 ml volumetric flask.

Transfer the stock solution to a 1000 ml class A volumetric flask. Rinse 100 ml flask with analyte-free water pouring the rinse into the 1000 ml flask.

Fill 1000 ml volumetric flask to the mark with analyte-free water.

Invert the 1000 ml volumetric flask several time s until the solution is homogeneous.

Label the storage container with “0.1M KCL Solution”, your initials, and the date of preparation and transfer the 0.1 Molar KCL stock solution to a storage bottle.

#### **5.4.8.3 Preparation of 0.01 Molar KCL standard solution**

Thoroughly mix the 1 Molar KCL stock solution by invert the storage bottle. Transfer about 25 ml of 1 Molar KCL stock solution into 50 ml beaker.

Measure out 10 ml of 1 Molar KCL stock solution using a class A 10 ml pipette equipped with a suction bulb. Transfer the 10 ml stock solution to a 1000 ml class A volumetric flask. Use a wash bottle containing analyte-free water; rinse the pipette over the 1000 ml volumetric flask. Invert the 1000 ml volumetric flask several times until the solution is homogeneous. Label the storage container with "0.01M KCL Solution", your initials, and the date of preparation and transfer the 0.01 Molar KCL stock solution to a storage bottle.

After you prepare the conductivity standards, you need to verify the specific conductance of the standard by checking against a certified, traceable standard from second source. Even you follow the procedure precisely; you may not get exact number listed in the table. But you should get number close to the true value. First, calibrate the instrument with the certified standard, then put the probe into the standard you made and record the number on the bottle. This should be the number you use to calibrate the Surveyor4. You do not need to adjust the standard to the true value.

## **5.4.9 Maintenance**

### **5.4.9.1 Dissolved Oxygen**

DO sensor maintenance is usually required when calibration becomes impossible or when the membrane covering the cell becomes wrinkled, bubbled, torn, dirty or otherwise damaged. Follow a regular schedule for membrane replacement.

Remove the O-ring securing the membrane. Shake out the old electrolyte.

Rinse the sensor cavity with analyte-free water. Refill with fresh D.O. electrolyte solution (2M KCL) until a perceptible meniscus of electrolyte forms above the entire electrode surface of the sensor. To remove any bubbles trapped in the electrolyte solution, tap gently on the side of the D.O. sensor.

To replace the membrane, hold both ends of the membrane between the thumb and index finger of both hands. Hold the membrane above the top and carefully drop the membrane over the top of the sensor.

Place the new O-ring over the gold cathode. Do not use any type of grease on the O-ring. Secure the membrane with the O-ring by pushing down with your thumbs on both side of the O-ring. Carefully trim the excess membrane extending below the O-ring with the pair of scissors or the pocket of knife.

Allow the membrane to relax two hours minimum, 24 hours recommended before calibration.

### **5.4.9.2 Conductivity**

To determine the appropriate maintenance, you need to carry out a periodic visual inspection of the sensor comparing your pre- and post-calibration results to the conductance standards used

Remove the screws securing the conductivity cellblock. Pull the cellblock out.

Remove the five small O-rings that are slipped over the electrodes. Polish the entire exposed surface of the electrodes with emery cloth strips. Be careful not to scratch the nearby pH glass electrode.

Replace the five O-rings.

Clean the electrodes and the cellblock with the brush and some methanol or a methanol-soaked cotton swab.

Rinse the electrodes and the cellblock with analyte-free water.

Wet the five O-rings with water to allow a better seal. Do not use any type of grease. Install the O-rings. Reinstall the conductivity cellblock. Insert and tighten the screws just enough to make sure that the cellblock is seated flat against the conductivity sensor body.

Rinse the sensor with analyte-free water twice. Let the sensor soak in tap water overnight to allow the freshly polished electrode surfaces to re-equilibrate with an aqueous environment.

### **5.4.9.3 pH Electrode**

The pH electrode obviously requires maintenance when coated with oil, sediment, or biological growth. Slow response or non-reproducible measurements are signs that the electrode has become coated or scratched.

Wet a cotton ball, swab, or a clean soft non-scratching cloth with methanol. Carefully clean the pH glass electrode. This procedure will help remove any film on the glass and restore the speed of response.

Rinse the electrode with analyte-free water

### **5.4.9.4 pH reference electrode maintenance**

Unscrew the Teflon junction. Pour out the old electrolyte solution.

Use a hypodermic syringe to rinse the reference electrode housing with standard electrolyte solution (3M KCL saturated with silver chloride). Pour out the solution and then use the hypodermic syringe to fill the housing with standard electrolyte solution. Make sure that no bubbles are trapped in the reference electrode housing after it has been filled.

Use a standard screwdriver to screw the Teflon junction back on.

#### **5.4.9.5 Temperature sensor**

Keep the temperature probe clean (free of barnacles or other deposits). Otherwise, the temperature sensor does not require any maintenance.

### ***5.5 Hydrolab Datasonde and Minisonde Multiprobe with Surveyor***

#### **5.5.1 Calibration of parameters**

##### **5.5.1.1 General procedures**

Perform the calibration and postcheck procedures specified below on each day of use.

DO NOT turn off the display unit at any time during the calibration procedure. The newly calibrated data will not be saved if the unit is turned off.

Maintain a calibration log sheet in which all data pertaining to each precalibration, postcheck, or maintenance procedures are entered.

Replace the storage cup on multiprobe with a bottomless calibration cup. Take special care not to bump the probes with your hand or the cup as this may result in damage to the probes.

After calibrating each parameter, record the calibrated parameter values in the calibration sheet (see Appendix A) and be sure to store the data utilizing the display unit.

When the surveyor internal battery reading drops below 7.2 volts, the surveyor internal batteries should be recharged.

Standards should be selected that best mimic the anticipated ambient sampling conditions.

### 5.5.1.2 Conductivity

Conductivity requires a two-point calibration. You need to calibrate your sensor to “0” first, then to the value of the slope standard you are using.

Dry conductivity probe opening with Q-tip or soft cloth.

Select “setup/cal”, “calibrate”, “sonde”, “SpCond:us/cm”, “Select”. Select the number 0 using the arrow key and select “done”. Press any key and select “go back”. SpCond will read 0.0.

Rinse with the conductivity standard you are using for the slope calibration. Discard the rinse solution.

Completely fill the calibration cup with fresh conductivity standard. The DO sensor must be covered. Allow the temperature equilibrate until conductivity reading are stable. Record the initial conductivity reading in the calibration log book.

If the circulator is not on, turn it on by selecting “setup/cal”, “setup”, “sonde”. Using the arrow key to choose “circulator: Off/On”, press “select”. Select the number 1 using the arrow key and select “done”.

Select “setup/cal”, “calibrate”, “sonde” then “SpCond: us/cm”. Using the arrow key, enter in the value of the standard in use and press “done”. Press any key and select “go back”. SpCond will read the value of the standard. Record the calibration conductivity value in the logsheet.

### 5.5.1.3 pH

Rinse the sensors with analyte-free water vigorously for 6 seconds. Discard rinse water.

Rinse sensors using the “zero” buffer (value between 6.8 and 7.2). Discard the rinse solution and fill the cal cup with fresh buffer solution. The pH sensor must be covered. Allow readings to stabilize and record the initial reading in the calibration logsheet.

Select “setup/cal”, “calibrate”, “sonde” then using down arrow key to find “pH:units” then “select”. Using the arrow key, enter the value of the standard being used and select “done”. Press any key and select “go back”. Allow the pH reading to stabilize. Record the calibration pH value in the logsheet.

Rinse the sensor with analyte-free water and discard.

Rinse with the pH buffer that will be used as a “slope” buffer (value either 4 or 10). Discard rinse solution. Fill the cal cup with fresh buffer solution, pH sensor must be

covered. Allow the pH reading to stabilize and record the initial reading in the calibration logsheet.

Select “setup/cal”, “calibrate”, “sonde” then using down arrow key to find “pH:units” then “select”. Using arrow key, enter the value of the standard being used and select “done”. Press any key and select “go back”. The pH reading must remain stable. Record the calibration pH value in the logsheet.

Once the pH calibration is completed, turn the power off and the Hydrolab is ready to use.

#### **5.5.1.4 Dissolved Oxygen**

Note: It is good practice to get the water to be used for precalibration from a carboy. The water will have stabilized to room temperature so the temperature equilibrium time will be reduced.

If the circulator is on, turn it off by selecting “setup/cal”, “setup”, “sonde”. Using the arrow key choose “circulator: Off/On”, press “select”. Select the number 0 using the arrow key and select “done”.

Fill the cap cup with water to just below the O-ring of the DO probe.

Using a kimwipe or other soft towel, carefully remove any water droplets from the DO membrane. Do not apply pressure to the membrane.

Cover the calibration cup loosely with the plastic storage lid, and allow the unit to equilibrate until the temperature reading is stable. Record the initial reading in the calibration log book.

Determine the temperature and Barometric pressure from the display unit and record the data in the appropriate spaces on the logsheet.

Select “setup/cal”, “calibrate”, “sonde”, “DO%: Sat” then “select”. Enter the value of the current barometric pressure in mmHG. Press any key and select “go back”.

Read the Oxygen concentration from the table based on temp in Celsius degrees as determined by the far left column and first row of the Saturated Dissolved Oxygen Chart (see Appendix B). Multiply the Oxygen concentration by the correction factor determined by barometric pressure (mmHg). The DO (mg/l) reading should be within  $\pm 0.2$  mg/l of the calculated saturated DO from the table.

Record both DO values (mg/l) in the logsheet.

Replace the storage cup.

Place a small amount of tap water in the storage cup to keep the DO membrane moist. Do not allow the water to come in contact with the sensors as an ionic gradient may develop resulting in dilution of the electrolyte solutions.

### **5.5.1.5 Thermistor Verification**

Central Office personnel will conduct temperature checks for multiprobes against an NIST certified thermometer annually when conducting site visits.

The temperature function for the Hydrolab is set at the factory and can not be calibrated and corrected in the field. There is no calibration procedure for temperature but rather verification. Regions should check the temperature probe against another multiprobe instrument's temperature probe semi-annually. If a discrepancy should occur (temperatures are not  $\pm 1^{\circ}\text{C}$ ) contact Central Office so that the probes can be checked against an NIST certified thermometer soon as possible. If there is good agreement between the instruments, then Central Office personnel will check the instruments against an NIST certified thermometer as planned.

The temperature verification should be conducted on three points such as an ice/water mixture (e.g.  $4^{\circ}\text{C}$ ) and at a warm water temperature that will best approximate the highest ambient temperature expected to be sampled (e.g.  $25\text{--}30^{\circ}\text{C}$ ) where the thermistor and/or certified thermometer are laid into the waterbath side by side and allow the temperature of water to stabilize before taking both of temperature reading. Send the Hydrolab unit back to the manufacturer for temperature calibration if the thermometer and Hydrolab values differ more than  $1^{\circ}\text{C}$ .

### **5.5.1.6 Barometric pressure sensor calibration**

To check if the Minisonde or Datasonde Barometric Pressure should be calibrated compare the instrument value to the barometric pressure in mmHg read from a NIST Traceable barometer. BP is measured by the Surveyor4 and used for depth and Dissolved Oxygen calculations. It needs to be checked against an NIST traceable barometer at least once a month. When the difference between Surveyor4 reading and traceable barometer is greater than 10 mmHg, the Surveyor4 needs to be calibrated to the traceable barometer. The traceable barometer needs to be calibrated annually.

If a barometer is not available it can be estimated using the following formula:  $\text{BP (mmHg)} = 760 - 2.5(A_{\text{ft}}/100)$  where ' $A_{\text{ft}}$ ' is the local altitude above sea level in feet.

If the BP value in the Surveyor differs from either the barometer value or the estimated value, the sensor needs to be calibrated.

For calibration, a corrected barometric pressure should be obtained from a barometer (mm Hg) or from the local weather bureau (inches Hg) (convert the inches of Hg to mm Hg by multiplying it by 25.4). Plug the corrected barometric pressure from the barometer or local weather bureau in mm Hg into the following formula to obtain the uncorrected BP that will be used in the calibration:

$$\text{uncorrected BP (mmHg)} = \text{corrected BP (mmHg)} - 2.5(A_{ft}/100)$$

To calibrate BP sensor:

Disconnect the surveyor from the datasonde/minisonde.

Turn on the surveyor.

Select "setup/cal".

Select "calibration".

Select "BP Svr4: User cal" and press select.

Using the arrow key, to enter the uncorrected BP in mmHg calculated above and press done.

### **5.5.2 Preparation for use**

If the short calibration cable is used for calibration, switch the calibration cable to a longer cable.

Remove the storage cup from the Sonde, screw on the sensor guard and store the Sonde in a moist environment when not in use.

### **5.5.3 Data Recording**

The field parameter data should be recorded and entered into CEDS to the tenth place (do not round based on the hundredth place).

### **5.5.4 DO calibration Confirmation**

A DO % saturation confirmation needs to be performed in the middle of run. The Hydrolab should be stored at 100% air/water saturation environment (e.g. wet towel or bottle with small amount water in it). Allow the probe to equilibrate, record the DO % saturation on the filed data sheet then transfer it to CEDS in the comment field. The

reading should be  $\pm 5\%$  of the true value. If DO % saturation is out of the specified range, the Hydrolab needs to be recalibrated in the field.

### 5.5.5 Maintenance and Postcheck

The Datasonde and Minisonde maintenance and postcheck procedures, postcheck criteria and are identical to those of the H20 model Hydrolab in Section 5.4.7 and 5.4.9.

### 5.5.6 Data Logging

Setting up a time triggered file in the Sonde with the Surveyor

- 1) Connect the Sonde to the Surveyor
- 2) Press files the Sonde
- 3) The option highlighted will be create
- 4) Press select
- 5) The next option will be time-trig
- 6) Press select again
- 7) You will be asked to name the file. Using the arrow keys, spell out the name. After naming the file you must press done.
- 8) You will then be prompted to enter the start date and time.
- 9) Enter you wish to start date and time, then ending with done to save your setting.
- 10) The next screen will ask you to enter the stop date and time.
- 11) You must enter your logging interval (HHMMSS).
- 12) You are asked for sensor warm-up time. This can be any length of time not less than 30 seconds and up to 2 minutes.
- 13) The next selection is the circulator warm up time. If you do not want to enable the circulator, you may enter 000000.
- 14) It will then ask you if you want the audio on or off.
- 15) The next screen will allow you to select the parameters you wish to record.
- 16) Using the down arrow key, stop at each parameter you wish to record and press add. After you have added all the parameters you wish to log, press done to save your selection.
- 17) You have completed setting up a logging file in the Sonde. You may now deploy the Sonde in the location you wish to monitor.

File transfer from Sonde to PC

- 1) With Sonde connected to computer
- 2) Select file
- 3) Transfer
- 4) Power down probe? Type N and enter
- 5) Select log file: type the number of the file you wish to download and enter.

- 6) Select spreadsheet
- 7) Select Xmodem
- 8) Screen will say starting Xmodem transfer.
- 9) Move you cursor to the top of the screen and open transfer.
- 10) Make sure you are using X Modem protocol.
- 11) Select receive file.
- 12) Now name the file using .csv extension.
- 13) Select OK
- 14) Transfer will begin.

#### Storing data in clipboard

If you surveyor has clipboard memory, you can store up to 12 scans by using the store function. This feature allows you to capture the lines of data displayed at the time you press the store key.

- 1) You need to select the parameters you would like to save to Surveyor clipboard.
- 2) Once you satisfied with your selection, press the done key and go back key three times.
- 3) Then press on the store key. You have now saved 1 scan to your surveyor.

#### Reviewing clipboard scans

- 1) From file, surveyor, clipboard screen, press select on review
- 2) Depending on the number of scans in the surveyor clipboard contains, you can press the down arrow key and move to the other files to review the information you stored earlier.

## **5.6 Quanta**

### **5.6.1 Calibration preparation**

1. Select a calibration standard whose value is nearest those expected to be observed in the field.
2. Clean and prepare the sensors.
3. Attach the calibration cup.
4. Using the calibration cap, thoroughly rinse the sensors several times by half-filling the calibration cup with analyte-free water and shaking the transmitter to make sure each sensor is free from contaminants that might alter your calibration standard.

5. In a similar manner, rinse the sensors twice with a small portion of calibration standard prior to calibrating with the standard discarding the rinse each time.
6. Discard used calibration standards appropriately. Do not attempt to reuse calibration standards.

## **5.6.2 Calibration**

### **5.6.2.1 Specific conductance**

1. Pour the specific conductance standard to within a centimeter of the top of the cup and make sure there are no bubbles in the measurement cell of the specific conductance sensor.
2. Selecting the Calib icon allows calibration of specific conductance. After selecting Calib, the Calib icon will remain lit in the operation icons and the parameter digits and units icons will be blank. The heading icons will display the items that can be calibrated.
3. From the displayed heading icons, select the item to be calibrated. The selected one will blink. The parameter digits show the current value for the item selected. Press the arrow to change the numeric value to match the calibration standard. Once the value is correct, press the enter key to send the updated calibration value to the transmitter

### **5.6.2.2 Dissolved Oxygen % Saturation**

1. Fill the calibration cup with deionized or tap water (specific conductance less than 0.5 ms/cm) until the water is just level with the O-ring used to secure the membrane.
2. Carefully remove any water droplets from the membrane with the corner of a tissue.
3. Turn the black calibration cup cover upside down (concave upward) and lay it over the top of the calibration cup.
4. Determine the barometric pressure for entry as the calibration standard.
5. Select the DO%/BP from Calib icon, enter barometric pressure and press the enter key.

### **5.6.2.3 pH**

1. pH is a two point calibration. A pH standard 7 is treated as the “zero” and all other values are treated as the “slope”. First calibrate “zero” then calibrate “slope”.
2. Pour the pH 7 standard to within a centimeter of the top of the cup.
3. Selecting “pH” from Calib icons. Press the arrow to change the numeric value to enter “7” and press enter key.
4. Rinse the transmitter with analyte free water thoroughly.
5. Pour the pH 4 or 10 standard to within a centimeter of the top of the cup.
6. Press the arrow to change the numeric value to enter “4” or “10” and press enter key.

### **5.6.3 DO calibration Confirmation**

A DO % saturation confirmation needs to be performed in the middle of run. The Hydrolab should be stored at 100% air/water saturation environment (e.g. wet towel or bottle with small amount water in it). Allow the probe to equilibrate, record the DO % saturation on the filed data sheet then transfer it to CEDS in the comment field. The reading should be  $\pm 5\%$  of the true value. If DO % saturation is out of the specified range, the Hydrolab needs to be recalibrated in the field.

### **5.6.4 Maintenance**

#### **5.6.4.1 Specific conductance**

1. Clean the oval measurement cell on the specific conductance sensor with a small, non-abrasive brush or cotton swab.
2. Soap or rubbing alcohol may be used to remove grease, oil or biological material.
3. Rinse with water.

#### **5.6.4.2 Dissolved Oxygen**

1. Remove the O-ring securing the DO membrane.
2. Shake out the old electrolyte and rinse with fresh DO electrolyte.

3. Refill with fresh DO electrolyte until there is a perceptible meniscus of electrolyte rising above the entire electrode surface of the sensor.
4. Make sure there are no bubbles in the electrolyte.
5. Hold one end of a new membrane against the body of the DO sensor with your thumb and with a smooth, firm motion, stretch the other end of the membrane over the sensor surface and hold it in place with your index finger.
6. Secure the membrane with the O-ring.
7. Make sure there are no wrinkles in the membrane or bubbles in the electrolyte.
8. Trim away the excess membrane extending below the O-ring.
9. Let the sensor soak overnight to allow the membrane to relax to its final shape.

### **5.6.4.3 pH**

1. If the sensor is obviously coated with oil, sediment or biological growth, clean the glass with a very clean, soft, non-scratching cloth wet with rubbing alcohol.
2. Rinse with tap water.

#### ***5.6.4.3.1 pH reference electrode***

1. Gently pull the entire reference sleeve away from the transmitter. The reference sleeve is the clear blue tube with a porous Teflon Reference Junction attached.
2. Discard the old electrolyte from the reference sleeve.
3. Drop two KCL salt rings into the reference sleeve.
4. Refill the sleeve to the top with reference electrolyte.
5. With the transmitter sensors pointed toward the floor, push the full reference sleeve back on to its mount until sleeve has just covered the first O-ring located on the mount.

6. Turn the transmitter so that the sensors point toward the ceiling and push the sleeve the rest of the way onto its mount.
7. Rinse with tap water.

#### **5.6.5 Postcheck check**

The Quanta postcheck check procedures and criteria are identical to those of the H20 model Hydrolab in Section 5.4.6.

### ***5.7 YSI 6-series Multiprobe Sonde with Data Logger***

#### **5.7.1 Scope and Application:**

The purpose of the following procedures is to provide guidance for calibrating YSI Sondes used to measure water quality parameters for surface ambient water. Water quality parameters include temperature, pH, dissolved oxygen, specific conductance, turbidity and Chlorophyll.

These procedures are written specifically for the YSI model 6-series Sondes (which include the 600XLM, 6820, 6920 and 6600 models) and YSI 650 MDS display system.

#### **5.7.2 Health and Safety Warnings**

- a. All the proper personal protective clothing and equipment are to be worn.
- b. The standard calibration solutions for conductivity, dissolved oxygen and the pH electrolyte solutions contain Potassium Chloride and the pH buffer solutions contain DI water, potassium acid phthalate, inert dye, potassium phosphate, sodium phosphate, potassium chloride and preservatives. When using the standards avoid skin contact, eye contact and ingestion. If skin contact occurs, remove any contaminated clothing immediately and wash the affected area thoroughly with large amounts of water. If eye contact or ingestion occurs, consult the Material Data Safety Sheet (MSDS) for prompt action and in all cases seek medical attention immediately.
- c. Rhodamine WT dye should be handled with care. The active ingredient in this dye is trimettlic acid. Very little is known about its long term effects on humans so it should be handled with care.

#### **5.7.3 Interferences**

### **5.7.3.1 pH**

- a. The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants or high salinity.
- b. Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, followed by distilled water rinsing. An additional treatment with Hydrochloric acid may be necessary to remove any remaining film.

### **5.7.3.2 Dissolved Oxygen**

- a. Dissolved organic materials are not known to interfere in the output from dissolved oxygen probes.
- b. Probes with membranes respond to a partial pressure of oxygen which in turn is a function of dissolved inorganic salts. Conversion factors for seawater and brackish waters may be calculated from DO saturation using salinity. Conversion factors for specific inorganic salts may be developed experimentally. Board variation in the kinds and concentration of salts in samples can make the use of membrane probe difficult.
- c. Reactive gases passing through the membrane probe may interfere with the probe's accuracy. For example, chlorine will depolarize the cathode and cause a high probe-output. Long term exposures to chlorine will coat the anode with the chloride of the anode metal and eventually desensitize the probe. Hydrogen sulfide will interfere with membrane probes if the applied potential is greater than the half-wave potential, an interfering reaction will not occur, but coating of the anode with the sulfide of the anode metal can take place.

### **5.7.3.3 Turbidity**

- a. The presence of floating debris and coarse sediments which settle out rapidly will give low readings. Finely divided air bubbles will affect the results in a positive manner.
- b. The presence of true color, which is the color of water due to dissolved substances absorbing light, will cause the turbidity to be low.

### **5.7.4 Equipment and Supplies**

NIST traceable thermometer  
pH buffer solution standards of 4, 7 and 10  
Conductivity standards

Turbidity standards  
Rhodamine WT dye  
DI and tap water  
Calibration cup  
YSI Sonde with attached pH, DO, conductivity, turbidity and Chlorophyll probes  
YSI display system  
Communication cable  
Calibration logsheet  
Disposable gloves and safety glasses  
Batteries

### **5.7.5 Procedure**

#### **5.7.5.1 Instrument Calibration**

The instrument must be calibrated prior to the sampling event.

Check the display/logger to determine the battery level to see if new batteries are needed.

During the calibration of the probes never accept any calibrations when a warning message has been given. You must determine the cause of the problem, correct the problem and recalibrate the probe before using the instrument.

Standards must be active (check expiration data) and fresh for all calibrations. Previously used standards may be used to rinse the probe but not for calibration. Discard and replace all expired standards.

#### **5.7.5.2 Dissolved Oxygen (DO)**

##### ***5.7.5.2.1 Rapid Pulse DO Probe***

The DO membrane and electrolyte solution should be inspected for any damage or air bubbles prior to calibration. If air bubbles or damage are present, replace the membrane according manufacturer manuals. To ensure accuracy wait 12 hours after changing the membrane before using the instrument to allow the membrane to equilibrate.

Invert the Sonde and clamp in the stand. Place approximately 3mm (1/8inch) of water in the bottom of the calibration cup. Make certain that the DO and temperature probes are not immersed in the water.

Engage only 1 or 2 threads of the calibration cup to insure that DO probe is vented to the atmosphere. Go to the Sondes "Report" menu and enable the "DO Charge". Now go to

the “Run” menu and start the Sonde in the “Discrete Run” mode at a 4 second rate and allow the Sonde to run (burn-in) for 10 minutes. Record the DO Charge after about 5 minutes. The number should be between 25 and 75. At this time the air in the calibration cup is water saturated and the temperature is equilibrated.

From the 650 MDS main menu press Sonde menu, select calibrate, select DO, then DO% to access the DO percent calibration procedure.

Enter the current barometric procedures (BP) in mm of Hg. The BP reading should be located at the bottom of 650 MDS screen.

Press Enter and current values of all enabled sensors will appear on the screen and change with time as they stabilize.

Observe the reading under DO%. When there is no significant change in the value for approximately 30 seconds, press enter.

The screen will indicate that the calibration has been accepted and prompt you to press enter again to return to the calibrate menu.

Record BP, temperature, calibrated DO in mg/l and 100% water-saturated air DO value (mg/l) in the calibration logsheet. The calibrated DO should be within  $\pm 0.2$  mg/l of saturated DO value. If not, recalibrate the Sonde.

Calculate the saturated DO value. Obtain the temperature and BP from the logsheet. Look up the 100% water saturated air DO table and figure out the DO value and correction factor. Multiply the Saturated DO value by the appropriate correction factor to determine the corrected saturated DO value. Record the corrected value on the logsheet.

When the calibration is complete, go to the Sonde’s “Advanced Menu” and then to the “Cal Constants” and record the “DO Gain”. The gain should be between 0.7 and 1.4. If the DO gain is out of range, the probe needs to be serviced.

#### ***5.7.5.2.2 Optical ROX DO Probe***

Place the sensor into a calibration cup containing about 1/8 inch of water. Vent the calibration cup by loosening the threads. Wait approximately 10 minutes before proceeding to allow the temperature and oxygen pressure to equilibrate.

Select calibrate from the main menu, and then select Optic T Dissolved Oxy.

Select DO%1-point to access the DO percent calibration procedure.

Enter the current barometric pressure in mmHg.

Press Enter and the current values of all enabled sensors will appear on the screen and change with time as they stabilize. Observe the reading under ODO%. When there is no significant change in the value for approximately 30 seconds, press enter. The screen will indicate that the calibration has been accepted and prompt you to press enter again to return the calibrate menu.

When the calibration is completed, go to the Sonde's "Advanced Menu" and then to the "Cal Constants" and record the "DO Gain". The gain should be between 0.75 and 1.25. If the DO gain is out of range, the probe needs to be serviced.

### **5.7.5.3 Conductivity**

Rinse the probe with DI water and then rinse with a small amount of the calibration standard to eliminate contamination.

Insure that the conductivity probe is completely submerged in standard solution. The hole in the side of the probe must be under the surface of the solution and not have any trapped bubbles in the opening. If bubbles are trapped on the conductivity cell, gently rotate and/or move the Sonde up and down to remove them  
Allow at least one minute for temperature equilibration before proceeding.

From the calibrate menu, select Conductivity to access the conductivity calibration procedure then select SpCond to access the specific conductance calibration procedure. Enter the calibration value of the standard you are using (mS/cm at 25°C) and press enter. The current values of all enabled sensors will appear on the screen and will change with time as they stabilize.

Rinse the Sonde with DI water.

When the calibration has been accepted, check the conductivity cell constant which can be found in the Sonde's "Advanced menu" under "Cal Constants". The acceptable range is  $5.0 \pm 0.45$ . Numbers outside of this range usually indicate a problem in the calibration process or that a contaminated standard was used.

### **5.7.5.4 pH**

Choose the appropriate standards that will bracket the expected values at the sampling locations.

Rinse the Sonde with DI water first then rinse with used pH 7 buffer solution, discarding the solution after rinsing. Fill the cup with the correct amount of fresh pH 7 buffer standard making sure that the temperature probe is submerged in the standard solution.

Allow at one minute for temperature equilibration before proceeding.

From Sonde menu, select calibrate, select ISE1 pH to access the pH calibration choices and then press 2 point. Press enter and input the value of 1<sup>st</sup> pH, press enter and the current values of all enabled sensors will appear on the screen and change with time as they stabilize in the solution. Observe the reading under pH and until there is no significant change for approximately 30 seconds. Press enter. The display will indicate that calibration is accepted.

Record the pH millivolts for pH 7 buffer solution. The acceptable tolerance for pH 7 buffer is  $0 \pm 50$  mv. When a probe is new, the ideal numbers are close to the 0, then as the probe begins to age, the number will move and shift to the higher side of the tolerance.

After pH 7 calibration is complete, press enter again to continue. Discard the pH 7 buffer, rinse the Sonde with DI water and then rinse with used pH 4 or pH 10 buffer.

Fill the cup with fresh pH 4 or pH 10 buffer to the appropriate level ensuring that the temperature probe is submerged in the standard solution.

Enter the value of 4.00 or 10.00. Press enter and the current values of all enabled sensors will appear on the screen and change with time as they stabilize in the solution. Observe the readings under pH and when they show no significant change for approximately 30 seconds press enter.

Record the pH millivolts for pH 4 or 10 buffer solution. The acceptable tolerance for pH 4 buffer is  $+180 \pm 50$  mv and 10 buffer is  $-180 \pm 50$  mv. When a probe is new, the ideal numbers are close to the 180, then as the probe begins to age, the number will move and shift to the higher side of the tolerance.

After recording the pH millivolts for the calibration points, you must determine the slope of the sensor. This is done by determining the difference between the two calibration points that were used. The acceptable range for the slope is 165 to 180. Once the slope drops below 165, the sensor should be taken out of service.

Discard pH 4 or 10 buffer solution and rinse the Sonde with DI water.

#### **5.7.5.5 Thermistor Verification**

- a. The temperature probe does not require calibration. The Sonde temperature probe needs to be checked for accuracy against a certified NIST traceable thermometer. This accuracy check should be performed at least once a year and the results of the check should be kept on file. Below is the verification procedure.

- b. The accuracy of the temperature probe must be verified by checking three temperature points (low, high and room temperature). For example, the low temperature should be around 4°C, the high temp around 32°C and the room temperature around 25°C. These ranges are the desired temperature ranges for the samples.
- c. Place Sonde and certified NIST traceable thermometer side by side into the water bath and wait for both temperatures readings to stabilize.
- d. Compare the two measurements. The instrument's temperature probe must agree with the certified NIST traceable thermometer  $\pm 0.5^{\circ}\text{C}$ . If the measurements do not agree, the Sonde's temperature probe may not be working correctly and the Sonde should not be utilized until it gets fixed.

#### **5.7.5.6 Barometric Pressure (BP)**

- a. Barometric pressure is measured by the 650 MDS data logger and used for depth and dissolved oxygen calculations. It needs to be checked with a NIST traceable barometer at once a month. When the difference between 650 MDS data logger BP reading and traceable barometer is greater than 10 mmHg, the 650MDS data logger need to be calibrated to the barometer. The traceable barometer needs to be calibrated annually.
- b. Once the uncorrected barometric pressure has been determined, the 650 MDS can be calibrated. In the main menu, select system set up and press enter.
- c. Using the down arrow, scroll down to calibrate barometer. Press enter.
- d. Record the Baro offset value.
- e. While the mmHg value is still highlighted, press enter. Key in the true barometric pressure. Press enter. Record the new Baro offset. The barometric pressure calibration is complete.

#### **5.7.5.7 Turbidity**

Turbidity is measured by a comparison of the intensity of light scatter of a sample under defined conditions to that produced by standard reference solutions. It is critical to the instrument's operation that the lens covering of the detection unit is kept clean during calibration and field use.

Check to make sure the turbidity probe and wiper are clean and free from any material.

Active the wiper to make sure it is wiping and parking correctly.

Allow the standard samples to equilibrate to the ambient temperature.

Clean all of the probes on the Sonde with DI water. Shake off excess water.

Place the Sonde in the black bottom calibration cup containing the 0.0 NTU standard (which can be DI water).

From the “Calibrate” menu, on the display unit, select the “Turbidity” option and press enter.

Select the “2-point” option and press enter.

Enter “0.0” as the first calibration standard and press enter.

Select the “clean optics” option to activate the automated wipers. Once the cleaning process is completed, wait for the turbidity measurement to equilibrate, and then press the enter key.

Place the probe in the second turbidity standard should be slightly above the highest concentration that is expected to be measured in the field.

Press enter to continue the calibration.

Enter the concentration of the second calibration standard and press enter.

Select the “clean optics” option to activate the automated wipers. Once the cleaning process is completed, wait for the turbidity measurement to equilibrate, and then press the enter key.

### **5.7.6 DO calibration Confirmation**

A DO % saturation confirmation needs to be performed in the middle of run. The Hydrolab should be stored at 100% air/water saturation environment (e.g. wet towel or bottle with small amount water in it). Allow the probe to equilibrate, record the DO % saturation on the filed data sheet then transfer it to CEDS in the comment field. The reading should be  $\pm 5\%$  of the true value. If DO % saturation is out of the specified range, the Hydrolab needs to be recalibrated in the field.

## **5.7.7 Troubleshooting**

### **5.7.7.1 pH**

If a probe is slow to respond, recondition the probe according to the “probe care and maintenance” in section 1.7

If the millivolts for each buffer solution or the slope between two buffer solutions is out of range as specified in section 1.6.1.3, the sensor should be replaced.

### **5.7.7.2 Dissolved Oxygen**

If the DO charge is out of range specified in section 1.6.1.1 the probe needs to be reconditioned following the instructions in section 1.7.

If the DO gain is out of range as specified in section 1.6.1.1 the probe needs to be serviced.

## **5.7.8 Logging Data**

Sonde can be used for to obtain discrete sample measurements or to be deployed for a period of time to obtain continuous measurements. Unattended deployment involves using the Sonde’s memory to log data. The display unit can be used to store data; however this requires the display to remain with the Sonde during monitoring.

### **5.7.8.1 Discrete sample measurement logging to MDS 650**

The first step in this application is to make sure that the sample interval is set correctly for the logging study. The default sampling interval is 1 second which needs to be changed to 10 seconds.

Highlight the logging setup in the main menu and press enter.

Press enter at highlighted interval selection and use the arrow keys to scroll to the right and change the interval from 1 second to 10 seconds. Confirm the selection by pressing enter and then press esc to return to main menu.

Highlight the Sonde run from the main menu and presses enter to begin data display.

Place the Sonde in the water and then highlight the start logging selection and press enter. The display prompts for a filename and site description. For our application, it is not

necessary to enter a filename or a site description. Highlight the OK window and press enter. The data will be logged to a file in the MDS 650 under the designation NONAME1.

The header of MDS 650 changes from logging to stop logging to confirm that the data storage to MDS 650 is active. When the measurement reading is steady, highlight the stop logging and press enter to terminate logging.

The file can be viewed by selecting file from the main menu and pressing enter. Next highlight the view file selection and then select the selected file and press enter. Use the arrow keys to scroll horizontally in order to view all of the data.

### **5.7.8.2 Deploying Sonde for Unattended Logging**

When calibrating the DO for unattended sampling that utilizes the auto sleep functions, the instrument should not be warmed up before calibrating (it should be calibrated when the instrument is cool).

From the Sonde menu, select the “Run/Unattended sample” option and press enter.

Follow the prompts on the screen to prepare the Sonde for unattended sampling including:

- Choosing sample interval time
- Logging start date
- Logging start time
- Logging duration (days)
- File name to store data
- Site name
- Battery life (make sure it will cover length of time monitoring)
- Memory space
- View parameters to log

Once these items have been correctly entered, toggle down to “start logging” and press enter. The display unit should show “stop logging”.

The Sonde will now begin logging parameters at the next sampling interval. Place the sensor guard on the Sonde. Turn the display off and disconnect the communication cable from the Sonde. Place the communication port plug on the Sonde. Place the Sonde in the desired sample location and securely anchor Sonde using the bail provided on the top of the Sonde.

The Sonde is now in place and will continuously record data until it reaches the specified logging end date and time.

### **5.7.9 Post Sampling Verification and Data Evaluation**

During use of the Sonde in the field, the instrument may experience “drift” and operate outside of the expected ranges. To determine the amount of drift the probes must be checked against the calibration standards at the end of sampling event.

#### **5.7.9.1 Dissolved Oxygen**

The dissolved oxygen should be checked in the field at approximately mid-day or in the middle of the run.

Place small amount of water in the bottle and place the Sonde into the bottle. Wait approximately 5 minutes for the air in the bottle to become water saturated and for the temperature to equilibrate.

Record the % dissolved oxygen on the field data sheet. The value should be between 95% and 100%. If the value is not within the specific range, recalibrate the instrument. Record the value in CEDS in the comment field.

Perform a postcheck at end of sampling event in the lab. Invert the Sonde and clamp onto the stand. Place approximately 3mm (1/8inch) of water in the bottom of the calibration cup. Make sure that the DO and temperature probes are not immersed in the water. Engage only 1 or 2 threads of the calibration cup to insure that DO probe is vented to the atmosphere.

Record the temperature, DO in mg/l and barometric pressure. The DO value should be within  $\pm 0.5$  mg/l of the saturation value (which is based on barometric pressure and temperature). If the data does not meet the criteria, the entire DO data collected on that day should not be recorded in CEDS.

#### **5.7.9.2 pH and conductivity**

Clean all the probes on the Sonde with deionized water. Rinse the probe with used standard calibration solutions.

Place calibration standard solution of particular parameter (e.g. pH, specific conductance, etc.).

Allow measurements to stabilize, record the data in the logsheet.

The post sampling verification data should be compared with QC limits listed in below table. If the data do not meet these criteria, the entire parameter data collected on that day should not be recorded in CEDS.

Parameter	post sampling verification criteria
pH	± 0.2 unit
conductivity (1.413, 12.90, 58.64 ms/cm)	± 10% of standard
conductivity (147 µs/cm)	± 5% of standard
Dissolved Oxygen	± 0.5 mg/l
Turbidity	± 20% of standard

## 5.7.10 Probe care and maintenance

### 5.7.10.1 DO probe

#### 5.7.10.1.1 Rapid Pulse DO probe

YSI recommends that the KCL solution and Teflon membrane should be changed at least once every 30 days or when calibration drift starts to exceed the criteria. In addition, the KCL solution and membrane should be changed if (a) bubbles are visible under the membrane; (b) significant deposits of dried electrolyte are visible on the membrane or the O-ring; and (c) if the probe shows unstable readings

After removing the used membrane, examine the electrodes at the tip of the probe. If either or both of the silver electrodes are black in color, the probe should be resurfaced using the fine sanding disks provided in the reconditioning kit.

To resurface the probe using the fine sanding disk, follow the instructions below.

First rinse the probe extensively with DI water and dry the probe completely with a cleaning tissue. Next, hold the probe in a vertical position, place one of the sanding disks under your thumbs, and stroke the probe face in a direction parallel to the gold electrode. The motion is similar to that used in striking a match. Usually 10-15 strokes of the sanding disk are sufficient to remove black deposits on the silver electrodes.

After completing the sanding procedure, repeatedly rinse the probe face with DI water and wipe with a cleaning tissue to remove any grit left by the sanding disk. Repeat this cleaning step at least three times to ensure removal of all sanding debris from the probe.

Install new KCL and a new membrane on the probe following the instruction in the operating manual and reinstall the probe into the Sonde bulkhead.

#### **5.7.10.1.2 Optical ROX Probe**

When the optical DO probe is not in use, it must be stored in a moist environment. It may be stored in water or in water-saturated air. Storage in water is preferable. The optical DO membrane may need to be replaced once a year in order to assure the maximum accuracy.

#### **5.7.10.2 Conductivity / Temperature Probes**

Dip the brush in clean water and insert it into each hole 15-20 times. In the event that deposits have formed on the electrodes, it may be necessary to use a mild detergent when brushing. After cleaning, check the response and accuracy of the conductivity cell with a calibration standard.

The temperature portion of the probe requires no maintenance.

#### **5.7.10.3 pH probe**

Cleaning is required whenever deposits or contaminants appear on the platinum surface of the probes or when the response of the probe becomes slow. Remove the probe from the Sonde and soak the probe for 30-60 minutes in 1M hydrochloric acid. Rinse the probe in clean water, wipe with a cotton swab saturated with clean water, and then rinse with clean water. To be certain that all traces of the acid are removed from the probe crevices, soak the probe in clean water for about an hour with occasional stirring.

Apply a very thin coat of O-ring lubricant to all O-ring before installation.

#### **5.7.11 Sonde storage**

##### **5.7.11.1 Short term storage**

The Sonde can be stored by placing approximately 0.5 inch of water in the storage cup. The use of a moist sponge instead water is also acceptable. The storage cup should be sealed to prevent evaporation.

### **5.7.11.2 Long term storage**

#### **5.7.11.2.1 600 XLM**

Remove the pH probe from the Sonde and store it according to the instructions in the following section. Cover the empty port with the plug provided. Leave the conductivity/temperature and dissolved oxygen probes in the Sonde with a membrane and electrolyte on the DO sensor. Place enough tap water in the calibration cup to cover the sensors, insert the Sonde into the vessel and seal with the cap to minimize evaporation.

#### **5.7.11.2.2 6600 EDS, 6820 and 6920**

Leave the conductivity/temperature and the dissolved oxygen probes in the Sonde with a membrane and electrolyte on the DO sensor. Remove all other probes from the Sonde and store according to the instructions found in the following section. Cover the empty ports with the plugs provided. Place enough tap water in the calibration cup to cover the sensors, insert the Sonde into the vessel and tighten the threaded cup to attain a good seal and minimize evaporation.

### **5.7.12 Probe storage**

#### **5.7.12.1 pH probe**

Remove the probe from the Sonde and seal the vacant port with the plug provided. Place the probe in the storage vessel used for the shipment of the Sonde. The vessel should contain a solution of 2 molar potassium chloride. Make sure that the vessel is sealed to prevent evaporation of the storage solution.

#### **5.7.12.2 DO probe**

Follow the manufacturer's instructions for long term storage of the Sonde.

### **5.7.13 Data and Records Management**

All the results of calibration, post sampling verification and field data sheet must be documented and kept in a safety place for five years. The field data should be recorded in CEDS at end of sampling event.

## **5.8 In-Situ Multiprobe Troll 9500 with Rugged Reader**

### **5.8.1 General procedures for calibration**

Perform the calibration and postcheck calibration procedures each day of the instrument is used.

Maintain a calibration logsheet in which all data pertaining to each precalibration, postcheck calibration or maintenance procedures are entered.

The calibration should reproduce anticipated field conditions as closely as possible, especially temperature. It is best to calibrate at the temperature that the sensor will be measuring.

The calibration cup's fill lines indicate the recommended amount of solution for most calibration, and ensure the temperature sensor is immersed. With a full complement of sensors installed, use the lower line as a guide. Except for the 100% dissolved oxygen calibration, the temperature sensor should be immersed in about an inch of fluid.

First rinse the sensors with tap water, then with distilled or analyte water followed by a rinse with the solution to be used for calibration.

There are three calibration status indicators. 1) Unstable: indicates the sensor response does not meet the criteria for a valid calibration point. 2) Nominal: indicates the sensor deviation meets early stabilization criteria. 3) Stable: displays when the readings have stabilized sufficiently to take a valid calibration point. The calibration proceeds automatically to the next screen.

Each time a sensor is calibrated, the information is written to the sensor, where it is stored until the next calibration.

After a certain amount of use the instrument will not be able to accurately calculate the calibration coefficients. The slope will gradually become lower and lower. At this point the sensor should be replaced

### **5.8.2 Calibration Procedure**

#### **5.8.2.1 Specific Conductance**

Remove the black PVC end cap from the calibration cup and screw the top of the stirrer to the bottom of the calibration cup.

Fill the calibration cup to the lowest fill line with solution.

Select MP TROLL 9000 in the navigation tree.

Select conductivity in the parameter list.

Select calibrate.

Select the calibration solution the sensor is soaking in. If the calibration solution concentration is not in the selection. Select other and enter the specific conductance of the solution in  $\mu\text{S}/\text{cm}$ .

Select next to continue.

In the next screen, select run to begin the stabilization.

When the sensor reaches the stable stage, the display unit will move to the final screen showing the new cell constant as calculated for the selected range during the calibration process.

Select finish to program the sensor with the displayed cell constant. The Kcell constant should range between 0.33-0.43. If the constant is out of the specified range check the sensor for fouling of the electrode.

Record the calibration conductivity value in the calibration logsheet.

The conductivity sensor is now calibrated and ready to use in the range for which it was calibrated.

### **5.8.2.2 pH**

Rinse the calibration cup with tap water, followed by distilled or analyte free water and first pH standard to be calibrated.

Fill calibration cup (with stirrer attached) with the standard solution to the lowest fill line. Select MP TROLL 9000 in the navigation tree.

Select pH in the parameter list.

Select calibrate.

Select the number of calibration points for this calibration, and the pH value of the calibration solution for each point. Since the range of pH encountered in the field may be unknown. A three point calibration is recommended.

Select next to continue.

Select run to begin the stabilization.

The wizard returns to the previous screen and waits for you to situate the probe in the next calibration solution.

Remove the calibration cup, discard the solution, rinse the calibration cup with tap water, analyte free water and the next standard solution. Refill the calibration cup with the next solution and attach it to the instrument.

Select run to begin the stabilization for the second calibration point.

Repeat step 9 and 10 for the third calibration point.

The final screen shows the sensor slope and offset calculated during the calibration process. For a 3-point calibration, two sets of calculated coefficients will be shown. Offsets calculated by the software for pH 7 will typically be between 390-450 mV. If the offset falls far outside these limits, it may be time to replace the sensor. The calculated slope will be typically between  $-54\text{mv/pH}$  and  $-62\text{ mv/pH}$ . A calculated slope greater than  $-50\text{mv/pH}$  or less than  $-66\text{mv/pH}$  may indicate the sensor needs replacing.

Select finish to program the sensor with the newly calculated calibration coefficients.

Record the pH 4,7,10 calibration values, the offsets and slopes on the calibration logsheet.

### **5.8.2.3 Dissolved Oxygen**

There are two methods to that can be utilized to calibrate DO. The traditional method, uses more stringent criteria, and is usually utilized for calibration for long-term deployment. The other method is quick calibration (QiKcal) which uses less stringent criteria and consumes less time for calibration.

#### ***5.8.2.3.1 DO traditional calibration***

Invert the TROLL so the DO sensor faces upward.

Fill the calibration cup (without stirrer attached) with water to just below the DO membrane.

Use soft swab or the corner of a tissue to remove moisture from the membrane.

Reattach the end cap loosely to insure the chamber is not pressurized. For proper venting, loosen the end cap until the small hole in the treads near the O-ring is at least partially visible.

Select the TROLL 9000 in the navigation tree.

Select Dissolved Oxygen in the parameters list.

Select calibrate.

If the instrument has a vented cable, choose use vented cable. Click OK to proceed.

Select continuous mode and one point calibration.

Click next to continue.

Select run to begin the stabilization for 100% DO calibration point.

The final screen shows the sensor slope and offset calculated during the calibration process. The slope of a properly functioning sensor should be between 25 and 35 nA/(mg/l). If the slope is slightly outside this range, repeat the calibration. The sensor may require further conditioning. Sensors that repeatedly fall outside this range may require a new membrane. The default offset for a one-point calibration is 2 nA. Offsets for two-point calibrations should be less than 10 nA.

Select finish, to program the sensor with the newly calculated calibration coefficients.

Record saturated DO from table, calibration DO and the DO slope on the logsheet.

The DO sensor is now calibrated and ready to use.

#### ***5.8.2.3.2 DO Quick calibration procedure***

Under parameter find QiKcal.

Press QiKcal.

Press stop.

Press back.

Uncheck pH sensor and Cond. Sensor.

Press run. Wait until it finished calibration.

The screen will ask you 'would you like to see the calibration report?' press yes

Scroll down to find and record temperature, stimulus DO(mg/l) and slope in the calibration logsheet.

Close the report

#### **5.8.2.4 Thermistor Verification**

Central Office personnel will conduct temperature verification against an NIST certified thermometer annually when conducting site visits.

The temperature function for the In-Situ is set at the factory and can not be calibrated and corrected in the field. There is no field calibration procedure for temperature but rather a QC check to verify the instrument is functioning properly. Regions should check the temperature probe against another multiprobe instrument's temperature probe semi-annually. If a discrepancy should occur (temperatures are not  $\pm 1^{\circ}\text{C}$ ) contact Central Office so that the probes can be checked against an NIST certified thermometer soon as possible. If there is good agreement between the instruments, then Central Office personnel will check the instruments against an NIST certified thermometer as planned.

The temperature verification should be conducted in an ice/water mixture (e.g.  $4^{\circ}\text{C}$ ), at a warm water temperature that will best approximate the highest ambient temperature expected to be sampled (e.g.  $25\text{--}30^{\circ}\text{C}$ ) and room temperature water where the probe(s) and/or NIST certified thermometer are laid into the water bath side by side and read. Send the In-Situ unit back to the manufacturer for temperature calibration if the thermometer and In-Situ values differ more than  $0.5^{\circ}\text{C}$ .

### **5.8.3 Set up**

The short calibration cable is just used for calibration; switch the cable to be utilized in the field.

Remove the storage cup from TROLL, screw on the restrictor and store the sensor in a moist environment when not in use

Profiling

At the station, turn on the IPQA.

Select MP TROLL 9000 in the navigation tree.

Select parameters in the navigation tree.

Select profiler to start the profiler.

After a moment, each active channel will be read sequentially, and the reading will be displayed. Readings are updated approximately every two seconds as the profiler cycles through the available channels in turn. The currently selected measurement unit is shown below each reading.

When you are ready to exit the profiler, click close. The parameter view will return to the screen.

### **5.8.4 DO calibration Confirmation**

A DO % saturation confirmation needs to be performed in the middle of run. The Hydrolab should be stored at 100% air/water saturation environment (e.g. wet towel or bottle with small amount water in it). Allow the probe to equilibrate, record the DO %

saturation on the filed data sheet then transfer it to CEDS in the comment field. The reading should be  $\pm 5\%$  of the true value. If DO % saturation is out of the specified range, the Hydrolab needs to be recalibrated in the field.

### 5.8.5 Loggin profiler data

To log a single set of profiler readings, click or tag the snapshot button in the view. The snapshot button flashes when logging. When it is done, it returns to not logging status.

Retrieving logged profile data:

Expand the data folder in the navigation tree by tapping the +.

Expand the node for the device type and serial number.

Look for the data file named with date and time of the profiler reading.

### 5.8.6 Postcheck

The postcheck calibration should be performed at the end of the run either in the office or in the field. Do not calibrate the instrument to the standard values during postcheck calibration procedure. A properly maintained instrument that is used on a regular basis should remain fairly stable and free from marked drift or variation in its measurements. Postcheck calibration of the instrument provides the user with immediate feedback on the instrument's general reliability and a written performance record for each of the parameters. Based on years of data, the following ranges are considered acceptable in day-to day instrument drift.

Dissolved Oxygen	$\pm 0.5\text{mg/l}$
pH	$\pm 0.2$ units
Conductivity (56.8 ms/cm)	$\pm 10\%$
Conductivity (12.90 ms/cm)	$\pm 10\%$
Conductivity (1.413 ms/cm)	$\pm 10\%$
Conductivity (0.147 ms/cm)	$\pm 5\%$

These ranges take into consideration real-world factors which a Unit is typically exposed to during the rigors of a day in the field (e.g. temperature extremes, rough rides in a truck etc.). Usually, a well-maintained instrument will demonstrate tighter agreement than the ranges listed.

Performance that falls outside of the acceptable ranges indicates the unit needs maintenance focused on the specific parameter that falls outside its range. If the performance remains substandard, the unit should be removed from service until it is repaired. It is highly advisable to have a backup unit available. The data collected during the sampling event is suspect and should not be keyed into the database or removed from the database.

## **5.8.7 Maintenance**

### **5.8.7.1 Removing sensors**

Sensors may be removed for inspection, cleaning, routine maintenance and storage. Remove a sensor by positioning the yoke of the sensor removal tool at the point where the sensor enters the sensor block. Firmly pry the sensor upward until it pops out.

### **5.8.7.2 Installing sensors**

Check lubrication of the sensor O-rings. The sensor O-ring requires generous lubrication before installation. If the O-ring appears dry, apply a silicone lubricant before installing.

Align the mark on the sensor with the alignment mark on the correct port.

Press the sensor with sensor insertion tool firmly into the port until it is securely seated. When properly inserted a gap of about 0.06" (width of the sensor removal tool) remains between the widest part of the sensor and the instrument body, for ease of the sensor removal.

### **5.8.7.3 pH sensor**

If a film develops on the glass electrode, the sensor response will tend to be sluggish. A deposit on the junction will result in an erratic response. In these cases, rinse the sensor in a detergent solution, then a rinse it in deionized water, and soak it in pH 4.00 buffer. This should restore the response. If not, sensor response may be restored by soaking in 0.1M HCl solution, followed by thoroughly rinsing. Soak the sensor in 2M KCL for at least an hour before calibration.

If the sensor glass should become dehydrated, performance can often be restored by soaking the sensor for at least an hour in pH 4.0 buffer or 2 M KCL. Check the reading after soaking for an hour or so. If the response has not improved, try soaking the sensor overnight and test again. If the response has still not improved, the sensor should probably be replaced.

### **5.8.7.4 Conductivity sensor**

Check the sensor for fouling of the electrodes. If necessary, flush the sensor with water, or swish in a mild detergent solution and rinse with tap water. A swab or soft bristle brush may be used to gently clean the electrodes. Remember that electrodes are made of graphite, which is soft and easily damaged.

### **5.8.7.5 Dissolved Oxygen sensor**

Inspect the sensor and membrane if readings begin to drift.

Check for discoloration of electrodes due to silver chloride deposition.

Inspect the membrane for integrity of the surface, for the presence of algal growth or other contaminants, for crystallization that may indicate a leak in the membrane, and to ensure there no air bubbles are trapped under the membrane.

#### Cleaning electrodes

Remove the membrane module and clean the electrodes as follows:

Cathode: use a polishing strip to buff the platinum cathode until it is shiny. This removes any deposits, increasing the chemically active surface of the electrode for a stronger DO signal.

Anode: remove silver chloride deposits from silver anode by cleaning with a soft bristle brush and ammonia. Excessive discoloration may be removed more easily by soaking for a half-hour in ammonia before cleaning with the brush. The surface of anode should appear uniform but not necessarily shiny. Regular cleaning will prevent pitting of the anode surface, caused by accumulated silver chloride deposition. Severe pitting can not be removed; the sole remedy is to replace the sensor. After cleaning, rinse thoroughly in analyte free water and shake dry.

#### Replacing the membrane module

Remove the sensor from the instrument. Remove and discard the used membrane module. Inspect and clean the sensor as needed.

Remove the soft protective cap from a new DO membrane module.

Holding the membrane module open-end up slowly fill the cap with electrolyte. Try to eliminate all air bubbles in the electrolyte –filled membrane module by tapping the side of the cap briskly with your fingernail.

Insert the clean DO sensor into the open end of the membrane module. To minimize the introduction of air, allow some of the electrolyte to overflow from the open end as the sensor is inserted. Ensure the membrane does not leak. You should not see any drops on the surface. When properly assembled, the membrane will bulge out slightly. There should be no visible air bubbles.

Thread the membrane module to the DO sensor.

Install and condition the sensor. Remember to condition the sensor at least overnight in continuous mode before recalibrating with a new membrane. Even with all visible air bubbles removed, a certain amount of gas will be trapped under the membrane. The conditioning period will remove this excess oxygen.

## **6 Dissolved Oxygen Method (Winkler Azide Modification Titration)**

### **6.1 Applicability**

This procedure is applicable to the analysis of dissolved oxygen in fresh, estuarine and coastal water samples. The results are measured and reported as mg dissolved oxygen /L of water.

### **6.2 Summary of method**

The iodometric test is the most precise and reliable titrimetric procedure for DO analysis. It is based on the addition of divalent manganese solution, followed by a strong alkali, to the sample in a glass-stoppered bottle. Dissolved Oxygen (DO) rapidly oxidizes an equivalent amount of dispersed divalent manganous hydroxide precipitate to hydroxides of higher valence states. In the presence of iodide ions in an acidic solution, the oxidized manganese reverts to the divalent state, with the liberation of iodine equivalent to the original DO content. The iodine is then titrated with a standard solution of Phenylarsine Oxide.

### **6.3 Health and safety warnings**

- It is important to wash your hands after handling laboratory chemicals. While some laboratory chemicals are not dangerous, many of those used with the Winkler method are poisonous or harmful to skin and/or clothing or both.
- Rubber gloves and safety glasses should be used.

### **6.4 Cautions**

Winkler titrations need to be conducted within 8 hours of fixing the sample. Samples should be fixed on site and stored in a box.

### **6.5 Interference**

There are a number of agents that may cause interference to the Winkler dissolved oxygen test, including iron salts, organic matter, excessive suspended matter, sulfide, sulfur dioxide, residual chlorine, chromium, cyanide and certain oxidizing and reducing agents.

Various modifications of the original Winkler procedure for DO have been developed to compensate for or eliminate interference. The Azide modification is for samples containing nitrate ions and ferrous irons.

## **6.6 Apparatus and materials**

### **6.6.1 Equipment**

1. Digital Buret
2. 300 ml glass stopper BOD bottle
3. 250 ml wide-mouthed Erlenmeyer flasks
4. 200 ml volumetric flask
5. Stirbar and stirbar retriever
6. Magnetic stirplate

### **6.6.2 Chemicals**

1. Hach Manganese Sulfate powder pillow
2. Hach Alkali-iodide-azide powder pillow
3. Hach Sulfamic acid powder pillow
4. Starch indicator solution
5. Phenylarsine Oxide 0.025N

Note: PAO is very poisonous. Care must be taken in handling this reagent.

## **6.7 Instrument or method calibration**

The digital burette should be calibrated following the manufacturer's instructions.

## **6.8 Sample collection**

Note: Winkler DO is usually taken for comparison purposes with a DO meter. Collect the Winkler sample at the same time and place as the meter readings is taken. If the meter reading is taken on a bridge, take the sample from the bucket. If the meter reading is taken in-stream, collect the sample in-stream. In-stream samples are preferred.

1. Rinse the BOD bottle twice with sample water, discarding the rinse.
2. Fill the bottle by tilting the bottle and submerging it under the water surface at an angle. Avoid introducing air bubbles into the sample by slowly turning the bottle up until it is filled and in an upright position.

### **6.9 Handling and preservation**

1. Immediately add 1 pillow of Manganese Chloride powder, followed by 1 pillow of alkali-iodide-azide powder.
2. Place the glass stopper onto the sample bottle carefully to avoid introducing air bubbles.
3. Invert the sample bottle until the most of the chemicals appears to dissolve. If air bubble appears in the bottle, recollect the sample.
4. When the precipitate has settled to at least half the sample bottle volume (leaving clear supernatant above the manganese hydroxide floc), mix the sample again by inverting the bottle several times.
5. Once the precipitate has settled to half the sample bottle for the second time, add a pillow of Sulfamic Acid powder to the sample, place the stopper on the bottle and shake well until the precipitate has dissolved. Occasionally, a dark brown precipitate persists in the bottle after acidification. This precipitate will dissolve if the solution is kept for a few minutes longer than usual. At this point the sample is considered "fixed" and concern for additional oxygen being introduced into the sample is reduced. Samples stored at this stage should be protected from strong sunlight and titrated.

### **6.10 Sample bottle cleaning**

- Sample containers must be clean, dry and free of contaminants. Using a lab grade detergent, wash with a good cleaning brush and rinse thoroughly with tap water followed by analyte-free water. Allow the bottle to dry in an upside-down position.
- All sample containers should be cleaned immediately after the test has been completed to prevent accumulation of residues in the containers, which can affect the test.

### **6.11 Sample analysis**

1. The titration must be completed within 8 hours of fixing the sample.
2. Prime the digital pipette before titrating to ensure there are no air bubbles in the pipette. Do this by drawing approximately 20 ml of 0.025N PAO into the digital pipette and then dispense all of solution into a beaker. Next pull approximately 20 ml of PAO into the pipette for the analysis. Zero the digital pipette.

3. Pour 200 ml of the sample from the BOD bottle into a 200 ml volumetric flask and transfer to an Erlenmeyer flask. Place the flask on the magnetic plate with stirrer in it and turn the stirrer on.
4. Titrate the sample with 0.025N Phenylarsin Oxide (PAO) until the solution is a pale yellow (straw) color. Add a small quantity of starch indicator drop by drop until the color of the solution turns blue.
5. Slowly titrate with the PAO until the blue color disappears. The titrated volume in ml is the concentration of Dissolved Oxygen in mg/l.

### **6.12 Data management and record management**

All records must be maintained in the logsheet and keyed into CEDS.

### **6.13 Quality Control criteria**

The difference between probe DO and Winkler DO should be within 0.6 mg/l.

### **6.14 Corrective Action**

If the difference is  $\pm 0.6$  mg/l or greater, most likely the membrane and electrolyte solution need to be changed. Change the membrane and electrolyte solution, recording the date of change on the maintenance sheet. Collect a Winkler sample on the next sampling run using that probe. If the difference between Winkler and the probe is less than 0.6mg/l, the problem has been resolved.

### **6.15 Reference**

Standard Methods for the Examination of Water and Wastewater, 18<sup>th</sup> edition.

## **7 Sample Identification and Corrective Action**

### **7.1 Field data sheet**

A field data sheet is required to be carried in the field by the sampler for each run. Make entries in the field data sheet for all the field parameters.

### **7.2 Sample label and tag**

The sampler should print the label from the pre-print label file in the computer. The label should have the following information: station ID, date collected, time collected, depth, unit code, collector, group code, preservative, lab processing code, blank/dup designation, priority and container number. The preprinted label should have filled in all the information except the collected time based on the monthly run information in CEDS. The collector fills in the time in the field using an indelible ink pen. The Avery label should be placed on the plastic or glass sample bottles or placed on a label that is then attached to the sample containers. When using cubitainers, the label needs to be placed on the sample tag that is then attached to the containers.

### **7.3 Corrective Action**

For the corrective action plan to be operative, all personnel associated with the program must report any suspected deficiencies in procedures or equipment. This is especially important for DEQ field personnel and DCLS lab personnel. Identification and correction of the problems in sample collection, preservation, handling and analysis is essential for an effective program.

The corrective action request (CAR) form (see Appendix C) is used to document the problem and steps taken for correction. CAR forms may originate in regions, central office or DCLS.

The originator:

- Identifies the problem.
- Lists possible causes (if known)
- Notes the date the problem was identified
- Identifies samples or field data that may be invalid as a result of the problem

- May recommend corrective action

CAR forms that originate in the region or central office are forwarded to the appropriate QA officer for review and recommendations. The QA officer forwards the form to the appropriate supervisor for review, recommendations and a final decision on appropriate corrective action. After resolution of the problem, the supervisor provides copies of the completed form to appropriate personnel on his staff and central office QA/QC officer. The supervisor has the responsibility for implementation of this corrective action. The QA/QC staff in central office may provide additional comments or recommendations to the supervisor for his review if requested.

CAR forms that originate in DCLS are forwarded to the central office QA officer for review, recommendations or concurrence. Then, if appropriate, these forms are forwarded to the appropriate supervisor for a final decision and implementation.

It is the responsibility of the originator to notify management and the QA officer in central office if the corrective action system is not operating effectively. In this situation, the originator may elect to call or send a CAR form directly to QA/QC central.

## **Appendix A**

### ***Calibration Logsheet***



## ***Hydrolab Multiprobe Calibrations and Postcheck Logsheet***

**Meter Series #** \_\_\_\_\_

Cal. Type	Date	Time	Temp.	Press. (mm Hg.)	Theor. (chart) DO	Meter initial DO	Meter Cal. DO	pH 7 init./ calib.	pH 4 or 10 init./ calib.	Cond. init./ calib.	Batt. Volt.	Init./Run ID
Pre  Post												
Pre  Post												
Pre  Post												
Pre  Post												
Pre  Post												



## In-Situ CALIBRATION AND POST CHECK LOGSHEET

SERIAL NUMBER: -

[illegible]



# YSI Calibration and Post Sampling Verification Logsheets

Model# \_\_\_\_\_ SS# \_\_\_\_\_

Calibration data

Date: \_\_\_\_\_

Time \_\_\_\_\_

Performed by \_\_\_\_\_

Sp. Cond (uS/cm)		pH (SU)				Dissolved Oxygen (rapid pulse probe)					
Cond.	Cell const. (4.55 - 5.45)	7		4 or 10 *		Temp	BP (mmHg)	Sat. DO value (mg/L)	Calibrated DO (mg/L)	DO Charge (25-75)	DO Gain (0.7 – 1.4)
		Value	Mv (-50 to 50)	Value	Mv						

\* pH 4 Mv between 130 and 230; pH 10 Mv between -230 and -130.

DO Gain for Optical Probe should be between 0.75 and 1.25.

Post verification

Date: \_\_\_\_\_

Time \_\_\_\_\_

Performed by \_\_\_\_\_

	Sp Cond (uS/cm)	pH (SU)		Dissolved Oxygen			
Accept Criteria	±10%	7	4 or 10	Temp.	BP (mmHg)	Sat. DO value (mg/L)	Meter DO (mg/L)
		±0.2	±0.2				±0.5 mg/L from Sat. DO
Value							

Calibration data

Date: \_\_\_\_\_

Time \_\_\_\_\_

Performed by \_\_\_\_\_

Sp. Cond (uS/cm)		pH (SU)				Dissolved Oxygen (rapid pulse probe)					
Cond.	Cell const. (4.55 - 5.45)	7		4 or 10 *		Temp	BP (mmHg)	Sat. DO value (mg/L)	Calibrated DO (mg/L)	DO Charge (25-75)	DO Gain (0.7 – 1.4)
		Value	Mv (-50 to 50)	Value	Mv						

\* pH 4 between 130 and 230 Mv; pH 10 between -230 and -130 Mv.

DO Gain for Optical Probe should be between 0.75 and 1.25.

Post verification

Date: \_\_\_\_\_

Time \_\_\_\_\_

Performed by \_\_\_\_\_

	Sp Cond (uS/cm)	pH (SU)		Dissolved Oxygen			
Accept Criteria	±10%	7	4 or 10	Temp.	BP (mmHg)	Sat. DO value (mg/L)	Meter DO (mg/L)
		±0.2	±0.2				±0.5 mg/L from Sat. DO
Value							



## **Appendix B**

### ***Saturated Dissolved Oxygen Chart***



Temp in °C	O <sub>2</sub> concentrations in mg/l									
	0	1	2	3	4	5	6	7	8	9
5	12.75	12.71	12.68	12.65	12.61	12.58	12.55	12.52	12.48	12.45
6	12.42	12.39	12.36	12.32	12.29	12.26	12.23	12.20	12.17	12.14
7	12.11	12.08	12.05	12.02	11.99	11.96	11.93	11.90	11.87	11.84
8	11.81	11.78	11.758	11.72	11.69	11.67	11.64	11.61	11.58	11.55
9	11.53	11.50	11.47	11.44	11.42	11.39	11.36	11.33	11.31	11.28
10	11.25	11.23	11.20	11.18	11.15	11.12	11.10	11.07	11.05	11.02
11	10.99	10.97	10.94	10.92	10.89	10.87	10.84	10.82	10.79	10.77
12	10.75	10.72	10.70	10.67	10.65	10.63	10.60	10.58	10.55	10.53
13	10.51	10.48	10.46	10.44	10.41	10.39	10.37	10.35	10.32	10.30
14	10.28	10.26	10.23	10.21	10.19	10.17	10.15	10.12	10.10	10.08
15	10.06	10.04	10.02	9.99	9.97	9.95	9.93	9.91	9.89	9.87
16	9.85	9.83	9.81	9.79	9.76	9.74	9.72	9.70	9.68	9.66
17	9.64	9.62	9.60	9.58	9.56	9.54	9.53	9.51	9.49	9.47
18	9.45	9.43	9.41	9.39	9.37	9.35	9.33	9.31	9.30	9.28
19	9.26	9.24	9.22	9.20	9.19	9.17	9.15	9.13	9.11	9.09
20	9.08	9.06	9.04	9.02	9.01	8.99	8.97	8.95	8.94	8.92
21	8.90	8.88	8.87	8.85	8.83	8.82	8.80	8.78	8.76	8.75
22	8.73	8.71	8.70	8.68	8.66	8.65	8.63	8.62	8.60	8.58
23	8.57	8.55	8.53	8.52	8.50	8.49	8.47	8.46	8.44	8.42
24	8.41	8.39	8.38	8.36	8.35	8.33	8.32	8.30	8.28	8.27
25	8.25	8.24	8.22	8.21	8.19	8.18	8.16	8.15	8.14	8.12
26	8.11	8.09	8.08	8.06	8.05	8.03	8.02	8.00	7.99	7.98
27	7.96	7.95	7.93	7.92	7.90	7.89	7.88	7.86	7.85	7.83
28	7.82	7.81	7.79	7.78	7.77	7.75	7.74	7.73	7.71	7.70
29	7.69	7.67	7.66	7.65	7.63	7.62	7.61	7.59	7.58	7.57
30	7.55	7.54	7.53	7.51	7.50	7.49	7.48	7.46	7.45	7.44

Barometric Pressure Correction factor:                      Conversion of inches Hg to mm Hg: use 25.4 as factor.

mm Hg	Corr. Factor	mm Hg.	Corr. Factor	mm Hg	Corr. Factor	mm Hg	Corr. Factor
775-781	1.02	750-746	0.987	725-721	0.953	700-696	0.92
770-766	1.014	745-741	0.98	720-716	0.947	695-691	0.914
765-761	1.007	740-736	0.973	715-711	0.94	690-686	0.907
760-756	1.0	735-731	0.967	710-706	0.934	685-681	0.90
755-751	0.993	730-726	0.96	705-701	0.927	680-676	0.893



## **Appendix C**

### ***Corrective Action Request Form***



## Corrective Action Request Form

Section I: to be completed by originator

Date:

Submitted By:

A. Nature of Problem:

B. Possible Cause:

C. Date of Problem Identified:

D. Samples That May Be Invalid:

E. Recommended Corrective Action (Optional):

Section II: to be completed by program manager

Date:

Name:

A. Recommended Corrective Action:

B. Follow Up Action Required:

C. Implementation Will Begin On:

Section III: to be completed by QA Officer

Date:

A. Recommended Corrective Action:

B. Follow Up Action Required:

C. Implementation Will Begin On:

## **Appendix D**

### ***Entering QA/QC into CEDS***



## Entering QA/QC data into CEDS

### QA/QC Run IDs:

QA/QC run IDs consists of the first letter of the region conducting the sampling followed by the letters QA and 2-letter program code under which the samples are collected (e.g. TQAAQ for Tidewater regional QA run for Ambient Monitoring Program).

### Blank/Dups designations:

R- Regular sample (default designation)

EB- Equipment Blank

S1- First sub-sample of a field split sample (these data are stored in the regular run ID)

S2- Second sub-sample of a field split sample (these data are stored in the QA/QC run IDs)

### Container number designations:

1 – 9 S1 sample containers

11 – 19 S2 sample containers (the ones place of a S2 container is the same as the corresponding S1 container e.g. if S1 for NUT4 is container number 2 then S2 for NUT4 is container number 12).

21 – 29 Equipment blanks (the ones place for equipment blanks also correspond to the S1 containers for the sample types e.g. S1 for NUT4 is 2 then EB for NUT4 is 22.)

### Lab Process code designations:

D - indicates to the lab to perform lab splits on the sample

M - indicates to the lab to perform matrix spikes on the sample

### Yearly run schedule:

- 1) In CEDS, click on applications /environmental monitoring/water/yearly run schedule.
- 2) In the yearly run schedule, set up a generic QA/QC run ID (e.g. TQAAQ).
- 3) Use QA as the station ID and survey program.
- 4) Enter the lab Proc Code for NUT4 and TNTUL containers as M.
- 5) Enter the appropriate depths (0 for EB), container IDs, parameter group codes and save. Once this is completed, the QA/QC run ID can be used for all QA sampling events.

Monthly schedule:

- 1) Click on applications/environmental monitoring/water/monthly run schedule.
- 2) Click on the get yearly run data tab.
- 3) Enter the regular run ID and the date to be collected on the first line of the pop-up screen. On the next line enter the QA/QC run ID (e.g. TQAAQ and the date to be collected).
- 4) Click on the get yearly run data button. The database will be automatically updated with the runs chosen and will be displayed in the monthly run schedule screen. Save.
- 5) Click on the query button.
- 6) Enter the regular run ID, the station chosen for QA/QC and the date as scheduled in step 5.
- 7) Change the blank/dups designation for all containers to S1.
- 8) Save.
- 9) Click the query button.
- 10) Enter the QA/QC run ID (TQAAQ) and the date scheduled in step 3.
- 11) Change the station ID from QA to the name of the station chosen for QA/QC sampling for all samples.
- 12) Change the blank/dup designation for all containers numbered 11-16 to S2.
- 13) Change the blank/dup designation for all containers numbered 21-26 to EB.
- 14) Save the information and exit CEDS.